On the Sorption of Water Vapour by Coal and its Spontaneous Heating

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1. Introduction

The effect of humidity on the rate of heat release due to oxidation of coal has been reported in an earlier communication(1). The results therein do not suggest that spontaneous heating in coal can occur due to oxidation reaction alone under normal ventilation practice. In the literature, however, frequent reference has been made by many investigators to the particularly humid conditions during heating incidents. Observations over a long period by Migdalski(2) and Wolowczyk(3) have revealed that in the Zwickau-Oelsnitz Coalfield in Germany the occurrence of spontaneous heatings coincided with the presence of high humidity in the mine atmosphere. According to Ashworth(4), humid air is "essential" for the starting of gob-fires. Mine fires have been reported starting at places where water issues in considerable quantity from the roof of the coal seam(3). The incipience of heating in stored coal especially after rainy weather is well known. According to Hoskin(5), fires in coal piles occur generally at the junction of wet and dry coals. Development of heating in the storage of coal-washery tailings has also been reported by Cabolet(6).

Earlier Winmill(7) and more recently Hodges and Hinsley(8) have reported that some dry coals catch fire when saturated oxygen is passed through them at 30°c, but the temperatures of the same coals rise only a little when dry oxygen is used. Subsequently, Hodges and Acherjee(9) have found that at a temperature of 30°c the heat release due to oxidation is very small in comparison with that due to sorption of water by the coal. Berkowitz and Schein(10) have commented that "the heat of wetting (or for that matter heat of condensation) may act as an important 'trigger'" in accelerating the oxidation of coal.

Although the above observations are useful in understanding the role of water vapour in the spontaneous heating of coal, the experimental conditions used in the tests fall far short of those generally found in practice. Extreme conditions of dryness and wetness of both coal and air (or oxygen) have been used in most cases. In practice, neither would the ventilation air in mines and the atmosphere in the vicinity of a coal pile necessarily remain saturated with water vapour, nor would the coal in question be dry all the time. Due to its hygroscopicity coal tends to remain in equilibrium with the surrounding atmosphere. If the humidity of the atmosphere increases, then the coal will take up some more moisture to achieve a new equilibrium. During the process of attaining equilibrium the coal undergoes certain chemical, physical and thermal changes. The present investigation is concerned with the estimation of thermal changes in various coals under such conditions. The coals equilibrated at a particular humidity have been subjected to air equilibrated at a higher humidity, and the heat release in coals has been estimated calorimetrically. Apart from the influence of humidity, the effects of some other variables on the process have also been studied.

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2. Experimental

The arrangement and operational procedure of the apparatus used in this investigation were similar to those described in an earlier paper(1). The additional feature was that after the whole system had attained stable thermal and hygrometric conditions, the flow of nitrogen was substituted by air of humidity higher than that with which the coal sample in the calorimeter had been brought to equilibrium. The experiments were carried out in an isothermal condition at 30°c, except on one occasion when the test was done at 35°c. The humidities at which these tests were performed were also the same as in the previous investigation. The data on the analysis of each of the eight coals used are given in Table 1. Generally, the coals were tested with samples of -72 mesh (B.S.S.), but to study the effect of particle size on the heating rate due to sorption of water vapour, four sized fractions of -25+36, -36+52, -52+72 and -72+200 mesh (B.S.S.) were prepared from the Coal F. Normal precautions using nitrogen were taken to avoid oxidation of the samples during their preparation and drying. In order to investigate the influence of weathering of coal on the process a few oxidised samples were prepared from the Coal H. A bulk sample of -72 mesh (B.S.S.) of this coal was oxidised at room temperature in dry condition by pure oxygen, and the sub-samples were subsequently withdrawn after 30, 50 and 70 days.

3. Results and Discussion

The progress of the experiments was registered by recording the output of the calorimeter, and the results were subsequently calculated from the thermograms. All the thermal data reported here are expressed on a dry coal basis, and the term "saturated" is used to state the equilibrium conditions of both coal and air at the particular relative humidity concerned. The Coals B, D, G and H were tested under several humid conditions using dry as well as moist samples. The rest of the experiments were done in one particular condition by passing air saturated with water vapour through dry coal at 30°c.

Tests with glass wool under extreme conditions showed that the rate of heat release due to sorption of water vapour by the small amount of glass wool, mixed with the coal samples during experiments, had a negligible effect on the results obtained with the coals.

The variation of the rate of heat release with time for each of the coals studied at different humid conditions is shown in Figures 1 to 3. A few tests were carried out to isolate the heating effect of oxidation from that of water sorption. In some of these experiments nitrogen was used throughout as the moisture carrier, and in others the flow of moist air was changed to moist nitrogen or vice versa in the course of a particular experiment. It appears from the results that at temperatures of 30° and 35°c the rate of heat release due to oxidation is very small in comparison to that due to the sorption of water vapour by the coal. The absence of any recognisable effect of oxidation under such conditions has also been reported by other investigators(9 & 10). It is known that coal sorbs a comparatively larger amount of water than oxygen, and that the heat of oxidation is much less than the latent heat of condensation of water vapour. According to Sevenster(11), coal sorbs water vapour at a much faster rate than it consumes oxygen. Therefore, it is expected that in above conditions the heat release due to sorption of water vapour becomes the rate-determining factor.

Tests with Dry Coals

The results of this series of tests are shown in Figures 1 and 2. It is seen that excepting the curve for the anthracite (Coal A in Fig.1) all other rate curves have the common feature of a peak at the early stage of experiment. With the introduction of moist air (or nitrogen) into the dry coal there occurs

a sharp rise in the rate of heat generation in the coal. After a short while it decreases for some time before rising again. It appears from Fig.2 that the height and shape of the initial peak are dependent on both the humidity of the moisture carrier and the type of coal. An attempt is made in a later section to explain the occurrence of this peak in the rate curves.

Scanning of the results reveals that the nature of the rate curve after the initial peak is related to the type of coal sorbing the water vapour. With the anthracite (Coal A in Fig.1) and high rank coal B (Fig.2) the rate of heat generation approaches the maximum value rapidly. However, it starts decreasing soon after at a faster rate, followed by a progressively slower rate. In the case of the medium and low rank coals (Coals C,D,E,F,G and H) not only does the rate reach the maximum gradually, but it also continues in that range for some time before decreasing slowly. This difference in the nature of the heating rate in various coals can be attributed to the difference in their hygroscopicity. From Fig.2 it is evident that with a particular coal the rate of heat generation increases with the increase in the saturation humidity of the atmosphere. This is discussed in detail in a later section.

Tests with Moist Coals

In this series the coals containing different amounts of moisture were subjected to moist air (or nitrogen) under conditions in which sorption of water vapour by the coals was ensured. The results, as plotted in Fig.3, show that the rate of heat release vs time curves do not have any initial peak as obtained in the previous series of tests. The curves for the tests with a particular coal, however, follow the general characteristics of those obtained after the initial peak during experiments with the same coal in dry condition. It is also evident that for each coal the rate of heat generation increases with the increase in the difference in the initial equilibrium humidities of the moisture carrier and the coal.

Influence of Various Factors on the Rate of Heat Release

The effects of several factors on the heating rate of coal due to the process under investigation have been studied on a common basis of comparison. The basis used is $Q_{t=20}$ cal/g of dry coal, the total heat produced in twenty hours of testing, and is termed the characteristic rate of heat release. In a few cases where the experiments have been terminated before twenty hours the $Q_{t=20}$ values are taken from the extrapolation of the respective graphs.

Influence of the Deficiency in the Equilibrium Humidity of Coal

The characteristic rates of heat release during various tests with each of the coals B, D, G and H are plotted against different values of e, representing the difference between the equilibrium humidities of the atmosphere and the coal, in Figure 4. In Fig.4(i) the results of the tests with dry coals are shown, and the $Q_{t=20}$ value at zero e for a particular coal is the characteristic rate of heat release during its dry oxidation(1). The results of the experiments with moist coals are illustrated in Fig.4(ii); and the corresponding $Q_{t=20}$ value at zero e for each coal is represented by the average of the $Q_{t=20}$ values obtained during oxidation of the coal in several moist conditions reported earlier(1).

It is seen in Fig.4 that the characteristic rate of heat release for each coal increases with the increase in the equilibrium deficiency of the coal; the relationship, however, is not directly proportional. This is as expected because of the fact that the coal-water sorption isotherms, obtained from the equilibrium moisture values at various relative pressures of water vapour, are

of sigmoid type. A comparison between the Figs.4(i) and 4(ii) show that in each case the rate of increase in $Q_{t=20}$ with e during the tests with dry coal is more than that obtained when the experiments were done with moist coal. To confirm this feature, however, it would be necessary to estimate the heat of sorption of water vapour by the coal during the process. The present experimental set-up precluded any such attempt.

Influence of the Rank of Coal

The general relationship between the characteristic rate of heat release due to sorption of water vapour and the rank of coal is illustrated in Figure 5. The $Q_{t=20}$ value for each coal in the above figure is taken from the result of the test with dry coal and air (or nitrogen) saturated at 100% R.H. at 30°c. The variations of the characteristic rate value with carbon and volatile matter contents of the coals are similar to those usually observed between the hygroscopic properties of coals and the parameters of coal rank. It appears, therefore, that the heat release due to sorption of water vapour in a coal is in general dependent on its hygroscopicity.

Influence of Coal Particle Size

Each of the four sized fractions of the coal F was tested under similar conditions. Dry samples of these fractions were subjected to air saturated at 100% R.H. at 30°c. The changes in the rate of heat release with time of sorption of water vapour by the sized fractions are shown in Figure 6. The curves are of similar nature, and there is a tendency for the rate to increase with the fineness of the coal particles. This feature is more prominent in Figure 7 where the characteristic rates are plotted against the average particle diameters. It is seen that while a decrease in particle diameter below about 358 microns has little effect on the characteristic rate, a significant decrease in the rate of heat release occurs when the particle sizes are increased from 358 to 511 microns.

The observed difference in heat release in various sized fractions of the same coal is due to the difference in the exposed external surface area of the samples. The common shape of the rate curves indicates that the mechanisms of the sorption of water vapour remain similar. The results also suggest that there may be a critical diameter of the coal particles below which any further sub-division has little effect on the rate of heat release. However, since only four tests were carried out it was not possible to find the point at which such distinct change takes place.

Influence of Weathering of Coal

For the purpose of investigating the effect of weathering on the heat generation in coal during sorption of water vapour, three oxidised samples of the coal H were tested under similar conditions. The rates of heat release in dry samples were measured when air saturated at 100% R.H. at 30°c was passed through them. The results are shown in Figure 8 together with those obtained during a similar test with the fresh sample of coal H. It is noticeable from the general feature of the curves that the mechanisms of heat release remain unaffected after weathering of the coal, although the rate of heat generation generally increases with the extent of weathering.

The equilibrium moisture contents of the above samples at the saturation vapour pressure at 30°c are shown in Table 2, together with the characteristic rates of heat release. Both the characteristic rate of heat release and the equilibrium moisture content increase with the period of weathering of the coal. The increased moisture retaining capacity of weathered samples is an established fact, and it is expected that there would be a corresponding increase in the total heat release at the end of the sorption process. The present data,

however, show that with the extent of weathering there occurs an increase in the rate of heat release in the coal too, and this is of particular significance to the problem of spontaneous heating.

The Initial Peak in the Rate of Heat Release vs Time Curves for the Tests with Dry Coals

In absence of any quantitative data on the amount of water sorbed by the coals, it is only possible to put forward some qualitative explanations, on the basis of the present results and the existing knowledge on coal structure, for the appearance of the initial peak in the rate curves obtained from the tests with dry coals.

From the past work(2) it is apparent that this peak is not directly related to the rate of sorption of water in the early period of the process. The absence of any peak in the rate curve for the test with the anthracite (Coal A in Fig.1) seems to confirm this. A broad comparison of the heat release in the initial stage, until the rate curve starts rising again, in various coals tested under similar conditions, shows that this amount generally decreases with the maturity of the coal. It is also noticed that this quantity increases with decrease in the average particle diameter of the coal (Fig.6). The occurrence of similar peaks during the tests with moist nitrogen and also with the oxidised samples rules out the effect of oxidation. The close similarity in shape between the rate curves after the initial peak for the tests with dry coals and those obtained from the experiments with the respective moist coals indicates that the dry coal surface is probably responsible for the appearance of the initial peak.

Young and Crowell(12) and Brunauer(13) have referred to the occurrence of similar initial peaks during sorption studies of some porous solids. They have explained it as the result of the heterogeneity of the sorbent surface which plays an important role, particularly at low sorbate pressures. Considering the heterogeneous nature of coal it seems reasonable that the above theory may also be applicable in general to the present observations. This theory, however, fails to explain not only the case of the anthracite, but also the observed initial peaks with the finer coal particles.

From the studies of coal constitution, it is known that the number of polar groups, such as -OH and =CO groups, in coal decreases with the maturity of the coal, and that these groups are almost absent in the anthracite(14). Evidence has also been put forward by a few investigators(15 & 16) suggesting that a part of the water in coal is held by forces other than physical. On the basis of these facts the present observations can be explained in the following manner.

During sorption of polar substances such as water there occurs immediate interaction between the water molecules and the active groups in coal, and thus more heat is liberated than that due to physical adsorption. As this preferential sorption proceeds and the most active sites become occupied, so the less active sites come into play resulting in lesser heat generation. With the progress of the process the rate of heat release starts increasing again as the phase changing of the water vapour takes place. Thus the observed difference in heat release during this early period of sorption of water in various types of coal is understandable. With the finer particles the active sites on the coal surface are more easily accessible to the water molecules and so an increased amount of heat release at the first stage is expected. More elaborate study is necessary for a complete picture of the phenomena involved.

4. Conclusions

It has been shown that under conditions where a coal is likely to sorb

water vapour, the chance of heating is more. In a humid atmosphere when simultaneous sorption of water vapour and oxygen takes place, the rate of heat generation in coal due to the sorption of water vapour becomes the rate-determining factor. For a given coal, this rate of heating has been found to reach the maximum within a few hours of the start of the process, and to increase with the increase in the equilibrium deficiency of the coal.

The variations of the characteristic rate of heat release during sorption of water vapour with factors such as rank, particle size and weathering of coal are observed to be related to the hygroscopicity of coal. This indicates that the causes of self-heating in coal are in part associated with its fundamental nature; it also explains the greater susceptibility of low rank coals towards spontaneous heating. The method used in this work is found suitable for this kind of work, and the results obtained can serve as a basis for further work.

Acknowledgements

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TABLE 1

ANALYSIS OF COALS USED

(As supplied by the N.C.B. Coal Survey Laboratories)

SAMPLE DETAILS			*ANALYSIS, PER CENT*							
			Air-dried					*dmmf* *		
Index	*Colliery*	*Seam*	*Moisture*	*Ash*	*V.M.*	*F.C.*	*Total S*	*V.M.*	*C.*	*H.*
A	Cynhaidre	Pumpquart	1.6	1.3	4.8	92.3	1.2	4.8	94.2	2.8
B	+	+	1.9	5.0	29.7	63.4	0.7	30.6	88.5	5.2
C	Easington	High Main	1.6	5.1	32.1	61.2	1.6	33.9	86.6	5.4
D	Thoresby	Top Hard	7.5	4.9	30.2	57.4	0.8	33.5	83.7	4.9
E	Bentinck	Yard	5.8	7.4	31.6	55.2	1.4	35.4	83.9	5.6
F	Whitewell	High Hazles	8.4	2.7	33.3	55.6	1.3	36.9	82.8	5.4
G	Denby Drury Lowe	Belpar-Lawn	4.6	7.5	34.2	53.7	1.9	39.9	81.5	5.8
H	Measham	Stockings	5.3	6.0	36.7	52.0	1.6	42.1	80.7	5.2

* Dry, mineral-matter free

\+ Supplied by Cardiff Coal Survey Laboratory, Sample No. CSL 2708

Table 2

Effect of weathering of coal on the equilibrium moisture content and the characteristic rate of heat release due to sorption of water vapour

Days of oxidation	0	30	50	70
Equilibrium moisture, % (w/w)	19.22	20.83	21.80	23.44
$Q_{t=20}$, cal/g (dry coal)	56.70	62.28	63.07	69.12

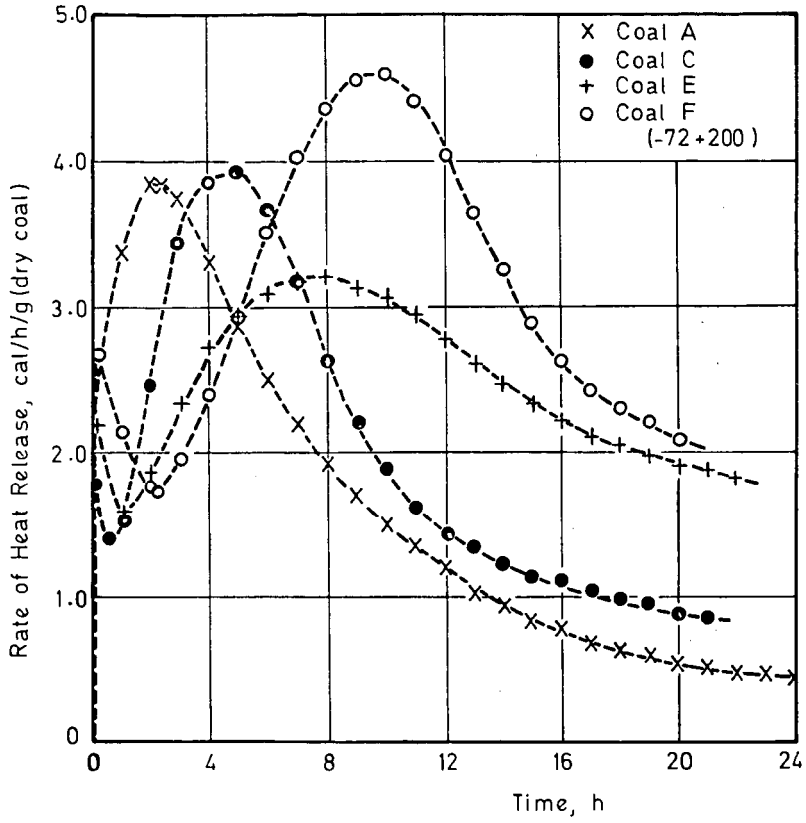


Figure 1. Variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coals.

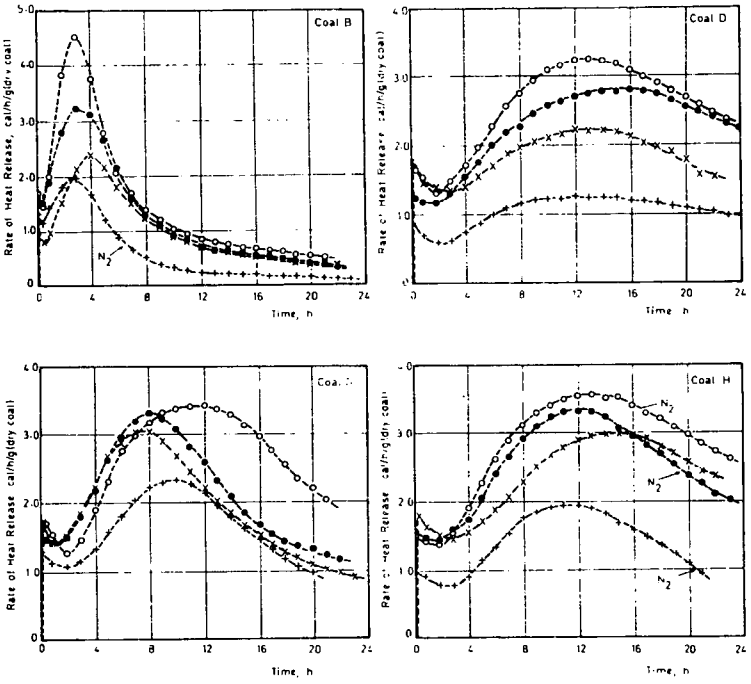
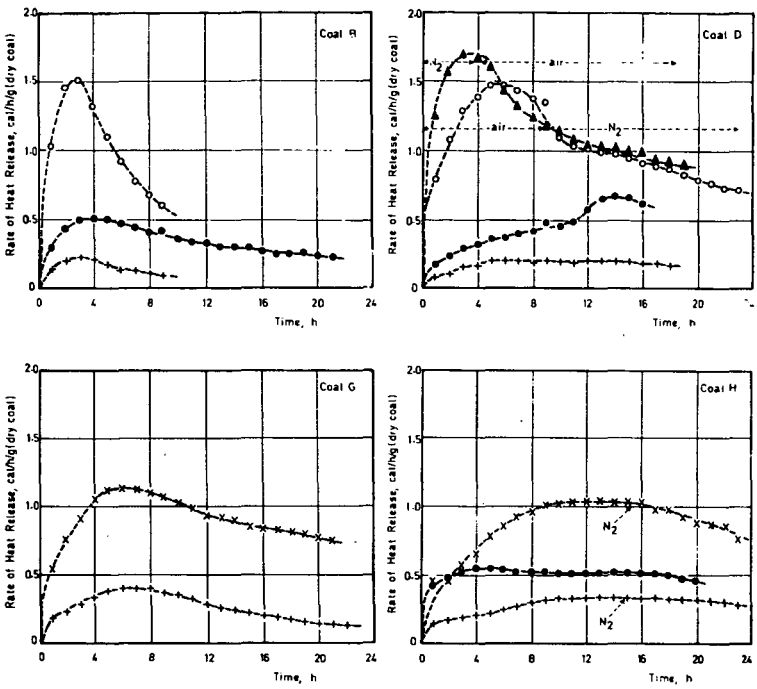


Figure 2. Variation in the rate of heat release with time during oxidation and/or sorption of water vapour by dry coals.



o Coal saturated at 43%R.H. and air/N_2 saturated at 100%R.H. at 30°c
x Coal saturated at 43%R.H. and air/N_2 saturated at 80%R.H. at 30°c
▲ Coal saturated at 43%R.H. and air/N_2 saturated at 80%R.H. at 35°c
● Coal saturated at 80%R.H. and air/N_2 saturated at 100%R.H. at 30°c
+ Coal saturated at 75%R.H. and air/N_2 saturated at 80%R.H. at 30°c

Figure 3. Variation in the rate of heat release with time during oxidation and/or sorption of water vapour by moist coals.

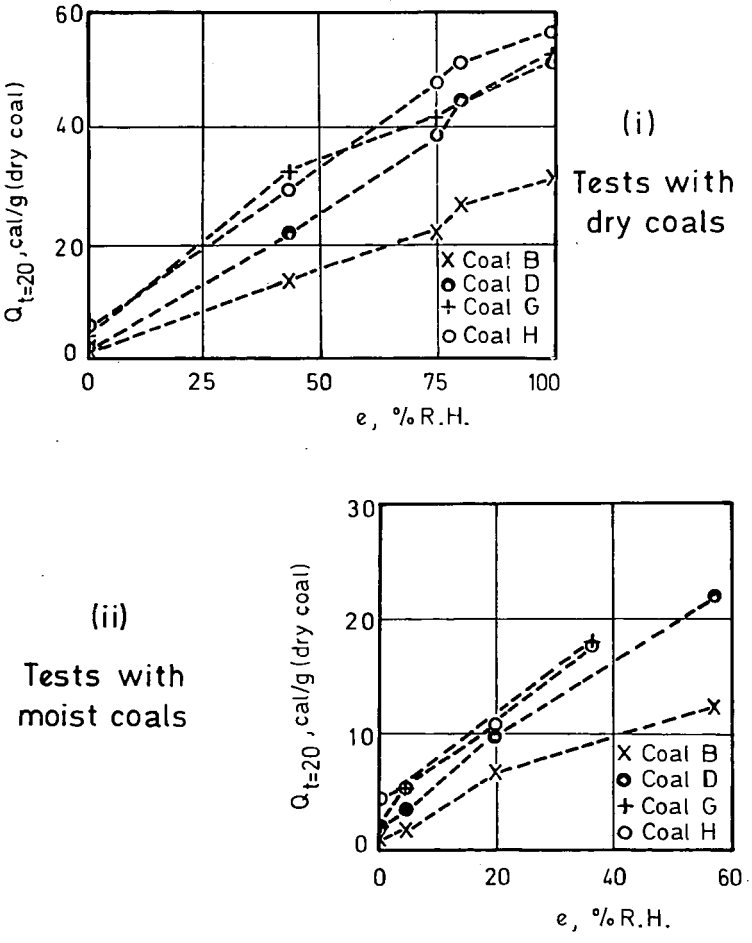


Figure 4. Variation in the characteristic rate of heat release with the equilibrium deficiency of the coals.

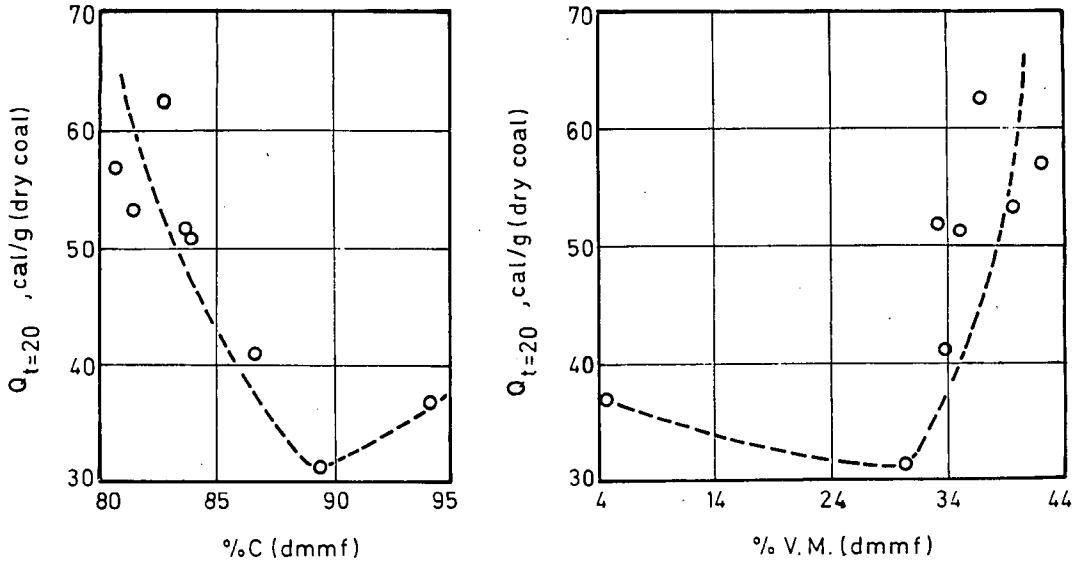


Figure 5. Variation in the characteristic rate of heat release with the rank of coal.

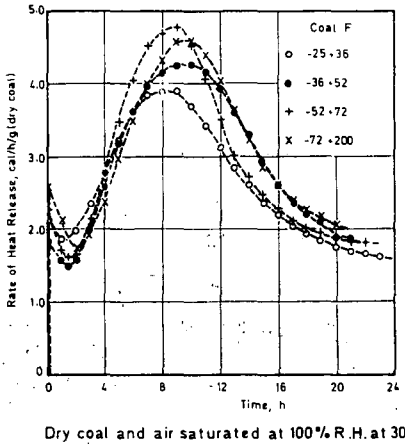


Figure 6. Effect of coal particle size on the variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coal.

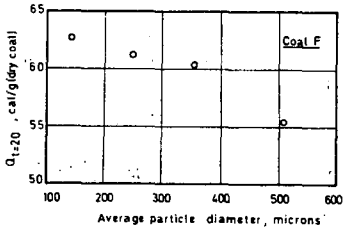


Figure 7. Effect of average coal particle diameter on the characteristic rate of heat release.

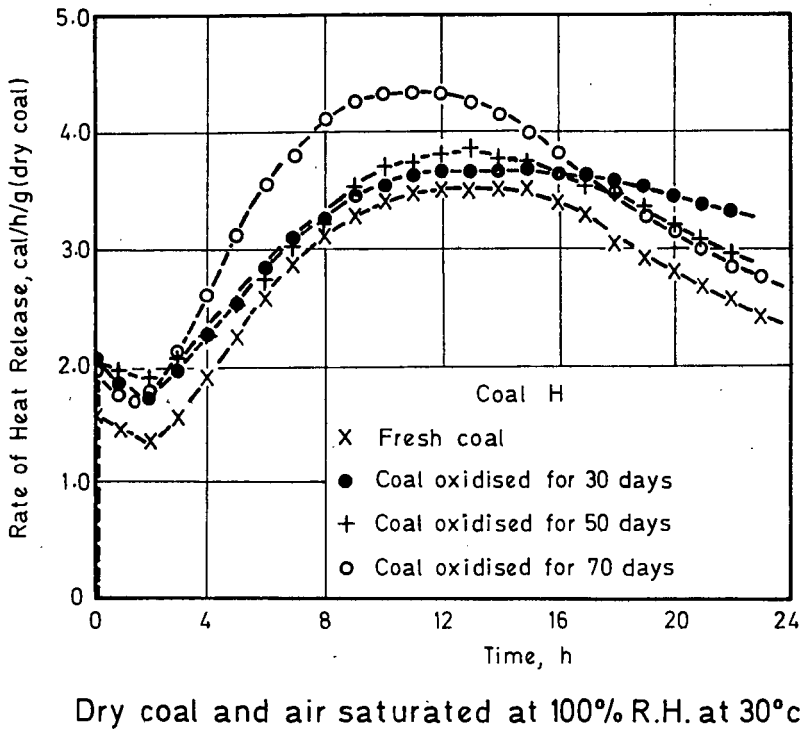


Figure 8. Effect of weathering on the variation in the rate of heat release with time during oxidation and sorption of water vapour by dry coal.

REFLECTANCE OF LOW-RANK COALS

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INTRODUCTION

The reflectance of the vitrinite in bituminous coals is very useful as an indicator of their rank and behavior in coking. Determination of reflectance might serve a similar purpose in the characterization of coal for hydrogasification; however, the relation of reflectance to rank of low-rank coal is not so straightforward. Moisture content has been reported to affect the determination of reflectance of Illinois coals, especially those having high surface areas.[1] Furthermore, in the study of the coals tested in our hydrogasification program, we have found that the reflectance does not always fall in line with the rank of the low-rank coals; thus, contrary to expectation, the reflectance of a Colorado subbituminous coal (0.52%) was higher than the reflectance of an Illinois high-volatile C bituminous coal (0.45%). This paper constitutes a progress report on our efforts to elucidate the parameters, including moisture content, that influence the reflectance of low-rank coal.

THEORY

The normal reflectance of the surface of a light-absorbing material such as coal is governed by Beer's relation:

$$R_o = \frac{(n_c - n_o)^2 + k^2}{(n_c + n_o)^2 + k^2}$$

where

R_o = reflectance in oil
n_c = refractive index of the material, here a coal constituent
n_o = refractive index of the immersion medium, here immersion oil
k = extinction coefficient of the coal constituent

Scattered light from beneath the surface has also been considered as a possible source of difference in reflectance between moist and dry vitrinite. Scattering increases with increasing difference in refractive index between the pore and the matrix, as when water in the pore is replaced with air. However, the extinction coefficients of these vitrinites are high enough that the beam of light can penetrate no more than a few microns, and the pores in question are so small that they are very inefficient scatterers. For these reasons it appears that back-scattering cannot contribute significantly to the reflectance.

McCartney and Ergun have determined refractive indices and extinction coefficients on vitrinites of a series of coals.[3] Among low-rank coals the extinction coefficient is low enough that it has only a small effect on the reflectance. Thus, its contribution to the reflectance of a Wyoming subbituminous coal is 0.026% out of 0.54% and to that of a high-volatile A bituminous coal is 0.24% out of 0.88%. Presumably the only significant source of any effect is the change in refractive index with change in the pore content of the submicroscopic pores.

The effect of density and pore content on the refractive index can be handled by the Lorenz-Lorentz relation in the form:

$$\frac{(n_c^2 - 1)}{(n_c^2 + 2)\, d} = r = w_1 r_1 + w_2 r_2 + \ldots w_n r_n$$

where

r = specific refraction
w_1, w_2, and w_n = weight fractions of components in the coal just beneath the surface
r_1, r_2, and r_n = specific refractions of components
d= apparent density with submicroscopic pores (but not larger ones) included in the volume

The relationships between reflectance and refractive index and between reflectance and refraction $[(n^2 - 1)/(n^2 + 2)]$ are shown graphically in Figure 1. These curves were obtained by setting the extinction coefficient in the Beer relation equal to zero, which gives us the well-known Fresnel relation. The actual reflectance of a coal of a given refractive index will be slightly higher than the calculated value from the graph.

To elucidate the effect of moisture and pore filling on reflectance, we need to know the fine porosity properties of the coal. These include true and particle densities, and the extent to which the immersion medium enters the pores.

EXPERIMENTAL

Pore Structure

Samples of high-surface-area Illinois coal were obtained from the Illinois State Geological Survey. Pieces of high vitrinitic content were picked from a sample from No. 2 seam, identified as IGS-IGT No. 1, by observation under a low-power microscope. These were crushed and screened to obtain a 40 to 80 -mesh USS sieve fraction. This particle size was chosen to be small enough to make a 5-gram sample representative and large enough to minimize error in the density determination, where the penetration of the interstices between fine particles by mercury is a problem. One portion of the sample was dried over a desiccant; another was treated with boiling water to fill its pores. The latter was then dried in a desiccator over potassium sulfate, the saturated solution of which gives an equilibrium atmosphere of about 96% relative humidity.

After the two samples had come to constant weight, particle density was determined on each sample by mercury displacement with a 6-ml Aminco penetrometer cell. The moist sample was cooled to about 0°C before evacuation to prevent appreciable loss of moisture. Volume readings and densities at 100 and 400 psig pressure were obtained; at 400 psig pores of the dry coal should be filled down to a diameter of 0.35μ. Moisture was also determined on these two samples; moisture, ash, carbon, hydrogen, and pyrite were determined on a separate sample ground to pass a 60-mesh sieve. True density was also determined on this sample by means of a Beckman air pkynometer with helium. Results are shown in Table 1, together with results of the calculation of densities and pore volumes to a mineral-matter-free basis.

Table 1. PORE VOLUME OF VITRINITE FROM AN ILLINOIS COAL

Sample	Moist 40-80 USS mesh	Dried 40-80 USS mesh	Ground <60 USS mesh
True Density, g/cu cm	--	--	1.291
Particle Density, g/cu cm			
Hg at 100 psig	1.252	1.109	
Hg at 400 psig	1.254	1.113	
Moisture, %	15.12	1.14	2.54
Composition (dry basis), wt %			
C			78.8
H			5.54
FeS_2			0.93
Ash			1.78
Moisture Content (mmf*), wt %	15.47	1.17	2.61
Particle Density (mmf), g/cu cm	1.236	1.094	--
Moisture (mmf), vol %	19.13	1.28	--
Porosity† (mmf), vol %	19.13	15.55	--
Pore Volume† (mmf), cu cm/g dry coal	0.183	0.144	--
Particle Volume (mmf), cu cm/g dry coal	0.957	0.925	--
True Density (dry and mmf), g/cu cm	--	--	1.280

*Mineral-matter-free.

†Including water volume. Normal density of water assumed.

According to the particle specific volumes (pore space included), it appears that the coal shrinks about 3% in volume when it dries. The "true" specific volume (pore space excluded) calculated from the particle density and moisture content of the moist sample agreed within 1% with the "true" specific volume of the dried sample determined with helium in the Beckman air pkynometer.

Reflectance

Moist and dry samples of the coal described above were prepared for reflectance determination by the method described by Harrison[1]. Cargille Type-B immersion oil was used. Other detailes of our apparatus for the determination are described elsewhere[2].

The results indicate no difference in reflectance between moist and dry samples. The reason for our failure to obtain Harrison's effect has not been discovered as yet.

DISCUSSION

Harrison[1] found differences in reflectance between moist and dry samples of about 0.1% on high-volatile C bituminous coals having high surface area; the dry samples gave the higher reflectances. With this in mind, it is instructive to calculate the change in reflectance to be expected if water in the pores is replaced with either air or immersion oil. From the measured reflectance of the moist sample we calculate its specific refraction and subtract the contribution of the water, assuming the specific refraction of the moisture in the coal to be equal to the specific refraction of bulk water. From the specific refraction on the coal itself thus obtained, we back-calculate the reflectance of the dry sample if oil does not enter the pores. Similarly, using the density and specific refraction of the oil as determined on a bulk sample, we can calculate the specific refraction and reflectance if the oil does enter the pores. We have done this for the sample on which the pore property and reflectance data above was obtained, with results as follows:

Observed Reflectance of Moist Sample, %	0.45
Calculated Reflectance, %	
Dried Sample, No Oil in Pores	0.22
Dried Sample, Oil in Pores	0.58

Thus, the difference in reflectance between the moist sample and the oil-filled sample is of the right amount and algebraic sign to agree with Harrison's results. However, further work is required to clarify conflicting results on the effect of moisture and to determine to what extent immersion oil enters the pores of low-rank coal.

ACKNOWLEDGMENT

This study was supported by IGT as a part of its in-house basic research program.

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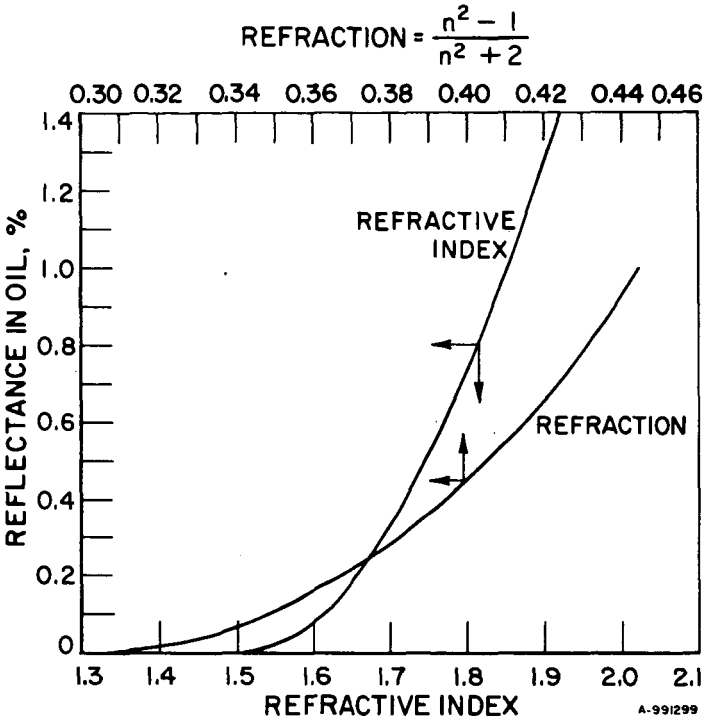

Figure 1. OPTICAL RELATIONSHIPS

THE STUDY OF COAL BY A SCANNING ELECTRON MICROSCOPE AND ELECTRON PROBE

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The object of this study of selected coal samples using a Scanning Electron Microscope (SEM) and Electron Probe (EP) was to ascertain whether coal macerals, normally observed by reflected light in an optical microscope, could be identified in the emission images of backscattered secondary electrons. As it was difficult to characterize finely disseminated mineral matter in coal macerals using an optical microscope, it was also important to explore the possibility of evaluating the distribution and chemical character of the mineral matter in the maceral types using the x-ray electron probe capability of the Philips SEM.

To compare the optical and SEM microscopes it was essential to select coal samples containing a wide variety of maceral types and to polish the surface to be examined as flat as possible. This was essential to prevent surface relief from contributing artifacts to the secondary electron emission. Everhart (1) has shown that changing the surface inclination to the beam by only a few degrees produces an appreciable change in the number of secondary electrons produced.

Kimoto and Russ (2) point out that the resolution of an image with a SEM is limited to the size of the area emitting photons or electrons at any moment. When the electron probe hits the specimen, scattering causes the probe to spread so that the final volume of electron capture is roughly teardrop-shaped as shown in Figure 1. Secondary electrons, with energies up to about 50 eV, are produced throughout this volume; however they are reabsorbed after travelling only about 100Å, so it is only the volume within 100Å or less of the surface that emits secondary electrons that can be detected. This volume is only a few tens of angstroms larger than the diameter of the incident probe which has not had much chance to spread. Hence the secondary electron image provides the highest resolution.

Backscattered electrons come from a greater depth, and hence from a point where the probe has spread further, so that the resolution of the backscattered image is poorer than the secondary electron image. Elements with high atomic numbers backscatter a greater fraction of incident electrons than ones with low atomic numbers.

The photons of x-rays or visible light come from essentially the entire teardrop volume and hence give the poorest resolution.

EXPERIMENTAL

A sample of Moss #3 coal was polished flat and examined with a Leitz Pan Pol Phot Microscope at a magnification of 450 using an air objective. Figure 2 shows a location selected for examination which contained vitrinite, semifusinite, and a large extremely dark wedge-like structure of what appears to be spore material, which could be readily identified by its wedge shape in the various other modes of examination in the scanning electron microscope. A comparison of Figure 2 with Figure 3, which was taken of the same location in the secondary emission mode, showed that dark bands of exinite (E) at the top of Figure 2 may be associated with similar dark bands at the top of Figure 3. The broad band of semifusinite (SF) in Figure 2 corresponds with a lighter region in Figure 3. The dark wedge-like structure of what appears to be spore material in Figure 2 seems to have an outer rim of high electron emission, as shown in Figure 3, with a characteristic dark thread-like structure midway between the two walls of the bright zone. Possibly this structure has a very high electrical resistance due to the high hydrogen content and thus builds up a negative charge that might reflect the electrons from the probe. The significance of this thread-like structure is not clear at present. The dark apparent voids in the semifusinite in Figure 2 do not correspond in shape with sufficient accuracy to be positively matched with the bright areas in the semifusinite in Figure 3.

Figure 4 shows the same location in the backscattered mode. The white areas in Figure 4 in the semifusinite correspond with the white areas in the secondary electron mode in Figure 3. The converse of this statement is not true. The definition is sufficiently sharp to permit the shapes of the white areas in Figures 4 to be accurately matched with those in Figure 3. The areas of high electron emission in the backscattered electron mode are thought to be due to mineral matter. The high electron emission of these particular areas is attributed to the much higher atomic number of the mineral matter as compared with that of the coal substance. It is noted that bright areas in Figure 3 do not necessarily correspond to bright areas in Figure 4. A striking example of this is the particle marked X.

This preliminary assessment was done using a Cambridge Scanning Electron Microscope which at the moment has no facilities for microprobe analysis. In

view of the importance of characterizing the mineral matter in coal, this preliminary investigation was extended using a Philips Model 4500 Electron Probe Analyzer with beam scanner.

A sample of coal from the Tantalus Butte Mine, N.W.T., Canada, was selected for examination for its relatively high concentration of semifusinite-containing mineral matter. This sample was polished flat and a location was selected that was approximately half vitrinite, and half semifusinite. This was done using a Leitz Microscope at a magnification of 300 with a water-immersion lens, Figure 5.

This same location was then examined in the backscattered electron mode and the resulting image, shown in Figure 6, reveals numberous light areas corresponding to the presence of the mineral matter in the semifusinite. On examining this same area with the microprobe analyzer using the first-order Si Kα line, the bright areas as shown in Figure 7 indicate the location of the silica. These areas of high silicon concentration are located in the region occupied by the vitrinite. With the Fe Kα first-order line, the bright areas correspond to areas of high iron concentration as shown in Figure 8. The area, in which the iron occurs, appears to be largely concentrated in the semifusinite regions of the field. Using the Ca Kα line from a mica crystal the distribution of calcium is shown to be concentrated in the semifusinite as may be seen from the location of the bright areas in Figure 9. Similarly, the carbon content was shown to be higher in the semifusinite region than in the vitrinite portion of the field, as may be seen in Figure 10. In this case, the CKα first-order line from a lead stearate crystal was used.

CONCLUSION

1. The macerals (vitrinite, exinite, fusinite, and semifusinite are visible in the secondary electron image. The indications are that the optical interpretation can be considerably extended by taking into account the differences observed between the secondary electron image and that obtained from back-scattered electrons.

2. The backscattered emission image generally indicates the presence of mineral matter in and between the maceral types.

3. The X-ray electron probe analyzer shows the iron and calcium to be concentrated in the semifusinite and fusinite portion of the field while the silica is concentrated in the vitrinite in the particular coal being studied. This tends to confirm the data recently obtained from washability studies that the high ash content is associated with higher concentrations of fusinite and semifusinite.(3)

4. The carbon content appears to be higher in the fusinite and semifusinite portion of the

portion of the field than in the vitrinite. This would be expected from the existing information on the chemical character of these macerals.

ACKNOWLEDGEMENT

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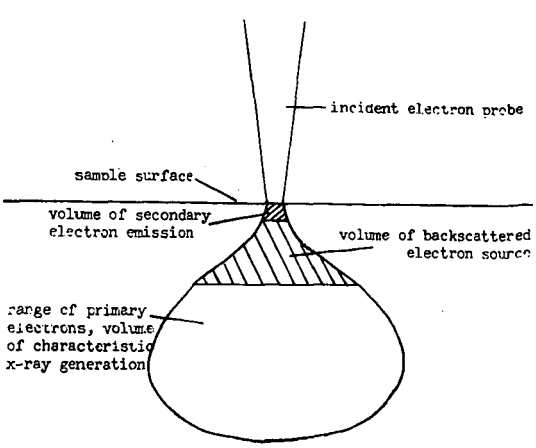

FIG. 1 Penetration of incident electron probe into sample.

FIG. 2 Optical micrographs of the macerals air objective reflected light X450.

FIG. 3 Scanning micrograph of the macerals of the same location as in Fig. 2 X400 approximately.

FIG. 4 Back-scattered electron micrograph of the same location as in Fig. 2 approximately X400.

FIG. 5 Optical micrograph of the macerals of coal from Tantalus Butte Mine; water immersion reflected light X300.

FIG. 6 Back-scattered electron micrograph of the same location as in Fig. 5, approximately X500.

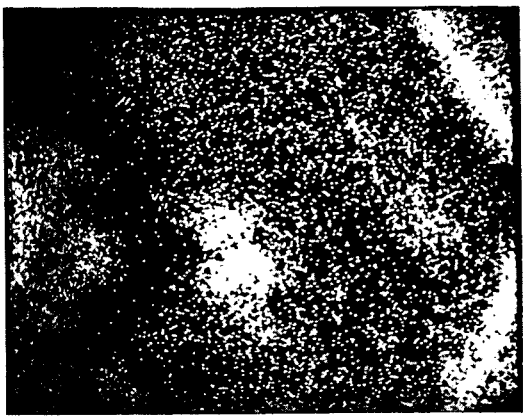

FIG. 7 Microprobe photograph of the silica X500

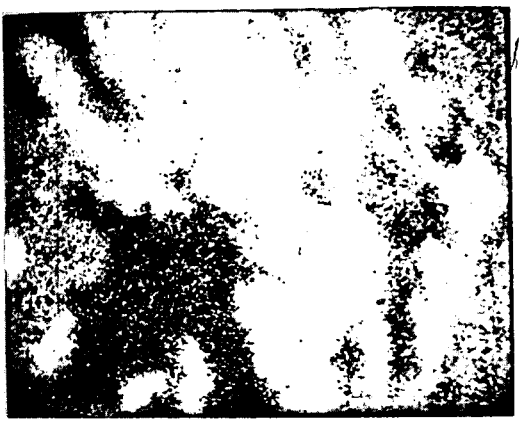

FIG. 8 Microprobe photograph of the iron X500

FIG. 9 Microprobe photograph of the calcium X500

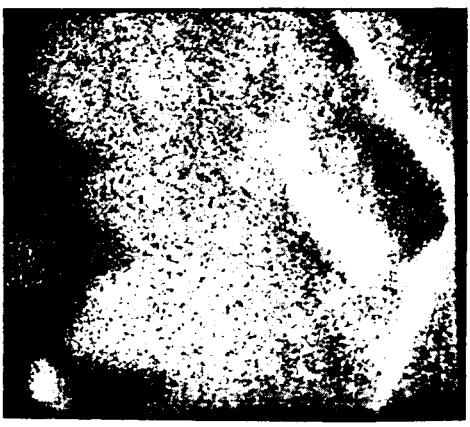

FIG. 10 Microprobe photograph of the carbon X500

ON THE SOLUBILIZATION OF COAL VIA REDUCTIVE ALKYLATION

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INTRODUCTION

We have recently shown (1) that treatment of Pocahontas (lvb) coal with alkali metal in hexamethylphosphoramide produced a "coal anion." The latter reacts readily with methyl iodide to give a methylated coal soluble in benzene at room temperature. We now present further work on the formation and alkylation of the coal anion.

EXPERIMENTAL DATA AND RESULTS

Reagents. Metallic potassium, naphthalene, alkyl halides, and tetrahydrofuran (THF) were of the highest purity available commercially. Potassium, naphthalene, and the alkyl halides were used as received. Tetrahydrofuran was purified by refluxing over potassium metal for 72 hr. followed by distillation under a protective cover of helium.

Coal. In all experiments, a hand-picked Pocahontas (lvb) vitrain sample, ground to pass 325 mesh, was used.

Petroleum Asphaltenes. The asphaltene sample was the pentane insoluble, benzene soluble (21%) fraction of a straight run residual asphalt of a California crude (85/100 penetration).

Formation and Titration of the "Coal Anion". Three anion species are produced when coal is treated with alkali metal in THF in the presence of naphthalene: naphthalene anion ($[C_{10}H_8]^-$), coal anion ($coal^{n-}$), and solvent anion ($\cdot CH_2(CH_2)_3O^-$). The latter is formed (2) by electron transfer from naphthalene anion to THF,

$$[C_{10}H_8]^- + THF \rightarrow C_{10}H_8 + \cdot CH_2(CH_2)_3O^- \quad (1)$$

Each anion, on treatment with water, liberates an equivalent amount of hydroxyl ion:

$$Coal^{n-} + nH_2O \rightarrow Coal\ nH + nOH^- \quad (2a)$$

$$[C_{10}H_8]^- + H_2O \rightarrow \cdot C_{10}H_9 + OH^- \quad (2b)$$

$$\cdot CH_2(CH_2)_3O^- + H_2O \rightarrow \cdot CH_2(CH_2)_3OH + OH^- \quad (2c)$$

The amount of hydroxyl ions formed can be readily determined by potentiometric titration with acid. By subtracting the equivalents of hydroxyl ions formed according to equations 2b and 2c from the total equivalents of hydroxyl ions, one obtains the equivalents of hydroxyl ions formed by the coal anion according to equation 2a. Knowing the amount and carbon content of the coal and the equivalents of hydroxyl ions formed according to (2a), one can calculate the number of negative charges associated with the coal anion in terms of negative charges per 100 carbon atoms.

In a typical experiment, under a protective cover of helium, a 250-ml Erlenmeyer flask provided with a glass enclosed stirring bar and suitable ground joint connections was charged with 120 ml of tetrahydrofuran (THF), 112 millimoles (4.4 grams) of potassium and 2.4 millimoles (0.304 gram) of naphthalene. The contents of the flask were stirred for 24 hr. A 1-ml sample of the dark green solution was withdrawn, placed in a 50-ml volumetric flask and diluted with water.

The aqueous solution was titrated with n/100 hydrochloric acid. To the dark green THF solution was added 6.17 grams of the vitrinite and stirring was continued for 72 hr. Every 24 hr. a 1-ml sample was withdrawn from the stirred reaction mixture and diluted with water to 50 ml. On addition of water, the coal anion suspension coagulates into a voluminous, brownish precipitate entirely different in appearance from the original coal. The aqueous mixture was allowed to stand for 48 hr. with occasional agitation to insure complete hydrolysis prior to titration. The results are summarized in Figure 1. Figure 1 shows that a sharp increase in the number of equivalents (43) takes place during the 24 hr. following the addition of coal. This increase is due mainly to the formation of coal anion,

$$nK^{\circ} + \text{coal} \rightarrow \text{coal}^{n-} + nK^{+} \qquad (3)$$

The increase of 9 equivalents occurring during the final 48 hr. of stirring is caused by the formation of anions produced by electron transfer from naphthalene anion to solvent (THF) molecules according to equation (1). The value of 43 equivalents obtained for the neutralization of the coal anion, in conjunction with the amounts of coal used (6.17 grams) and the carbon content of the coal (88.3%), leads to the conclusion that the coal anion derived from Pocahontas coal contains 9.5 negative charges per 100 carbon atoms. The value of charges per 100 carbon atoms obtained in six separate titrations of freshly prepared coal anion suspensions varied from 9.5 to 12.1. The average value of these six titrations was 10.7 negative charges per 100 carbon atoms.

Alkylation of the Coal Anion. Under a protective cover of helium, the coal anion suspension described above was removed from unreacted potassium and was placed in an Erlenmeyer flask provided with a glass enclosed stirring bar. The flask was cooled in an ice bath. A solution of 10 ml of C-14 labelled ethyl iodide in 30 ml THF was added dropwise to the stirred dark red, almost black coal anion suspension in the course of 30 min. The mixture was allowed to warm to room temperature as stirring was continued for 2 hr. During this period the mixture became dark brown. The contents of the flask were poured into 600 ml of ethanol and the alkylated coal was separated by centrifugation. The supernatant ethanol solution was decanted and the residue treated with fresh ethanol. Treatment with ethanol and centrifugation was repeated until a sample of the ethanol washing was free of iodide ion. The precipitate was then repeatedly treated with water and centrifuged to remove any water soluble material. Finally, the precipitate was dried in vacuo at 100° to constant weight. The dried, treated coal weighed 6.03 grams. Taking into account the amount of coal withdrawn for titration (0.23 gram) and the amount of ethyl groups (8.8) added per 100 carbon atoms (see below), this corresponds to a recovery of 86%. The C-14 activity of the ethylated coal expressed in dpm/mg (decompositions per minute per milligram) was 3.09×10^3 and that of the ethyl iodide (in dpm/ml) was 7.05×10^6. The C-14 activity of the coal was determined by combustion analysis and that of the ethyl iodide by direct liquid scintillation analysis using an internal standard. On the basis of these data, the ethylated coal contained 8.8 ethyl groups per 100 carbon atoms. In similar experiments, coal was alkylated with C-14 methyl iodide and also with unlabelled normal butyl iodide. Radioactivity and combustion analysis of the methylated coal showed that the latter contained 8.1 methyl groups per 100 carbon atoms. Analyses of the original coal and alkylated coals as well as those of the benzene soluble and benzene insoluble fraction of the methylated coal are shown in Table 1. Hexane and benzene solubilities at room temperature (Table 2) were determined by tumbling 0.1 gram of alkylated coal and 15 ml of solvent in a sealed test tube for 1 hr. and centrifugation of the undissolved coal. This process was repeated two more times and then the residue was dried in vacuo at 100° to constant weight. The benzene soluble fraction of the methylated coal was practically free of ash (0.03%) while the original coal

contained 1.97% ash. In contrast to ethylated and butylated coal which were 95 and 93% soluble in benzene, methylated coal was only 48% soluble in benzene. Based on C-14 analysis and carbon content of the benzene soluble and benzene insoluble portion, the benzene soluble portion contained 8.4 methyl groups and the benzene insoluble portion 7.4 methyl groups per 100 carbon atoms. Infrared spectra (KBr pellet) of the alkylated coals showed strong bands at 3.4 μ and 7.25 μ attributable to the methyl group and the associated stretching vibration. The intensities of these bands in the original coal were only about one tenth of those found in the alkylated coal.

TABLE 1. Ultimate analyses of alkylated coal

	C	H	N	S	O[1/]	I	Ash
Original coal	88.25	4.55	1.19	0.57	3.47	.00	1.97
Methylated coal	87.22	6.03	1.14	.13	3.34	.00	1.54
a. Benzene soluble fraction	89.40	6.34	1.15	.06	3.02	.00	.03
b. Benzene insoluble fraction	85.71	5.43	1.09	.30	4.33	.00	3.14
Ethylated coal	87.81	6.33	.94	.37	2.52	.02	2.02
Butylated coal	87.24	7.23	.90	.31	2.17	.08	2.08

1/ By difference.

TABLE 2. Solubility of the alkaylated coal

	Percent soluble	
	Hexane	Benzene
Original coal	nil	0.5
Methylated coal	3	48
Ethylated coal	11	95
Butylated coal	17	93

Molecular Weight Determinations. Number average molecular weights of the benzene soluble portions of alkylated coals and, for comparison, of one sample of petroleum asphaltenes, were obtained by vapor pressure osmometry. Four samples, ranging in concentration from 5 to 35 grams per 1000 ml of benzene were used in each determination and the molecular weight at infinite dilution was obtained by the method of least squares. A typical plot of molecular weight vs. concentration is shown in Figure 2. The results are summarized in Table 3 along with the molecular weights calculated on an alkyl-free basis. In calculating the molecular weight of butylated coal on a butyl-free basis, it was assumed that the butylated coal contained the same number (8.8) of alkyl groups per 100 carbon atoms as the ethylated coal.

TABLE 3. Number-average molecular weights of alkylated Pocahontas vitrain and petroleum asphaltenes

	Number-average molecular weight	
	Found	Calculated for alkyl-free coal
Ethylated coal	3300	2800
Butylated coal	4100	3000
Petroleum asphaltenes	4200	

DISCUSSION

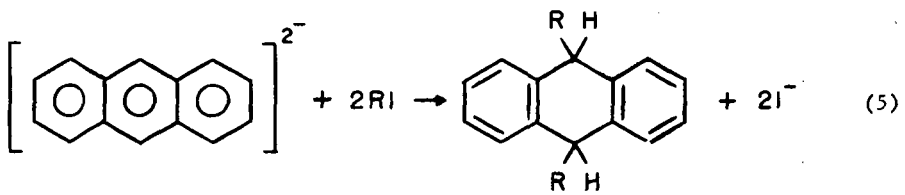
Formation of the "Coal Anion." Pocahontas vitrinite, when treated with potassium in tetrahydrofuran in the presence of a small amount of naphthalene, is converted to a coal anion. An electron transfer agent such as naphthalene is required because neither potassium nor coal are soluble in THF. Naphthalene, being soluble in THF, readily reacts with K° to form the anion $[C_{10}H_8]^-$. The latter is a strong electron donor and transfers its charge to the polycyclic aromatic hydrocarbons in coal as illustrated in equation (4)

$$K^\circ + C_{10}H_8 \rightarrow [C_{10}H_8]^- + K^+ \qquad (4)$$

$$[C_{10}H_8]^- + \text{coal} \rightarrow C_{10}H_8 + \text{coal}^-$$

By this method, a large amount of coal can be converted to coal anion in the presence of a small amount of naphthalene. The number of charges associated with the coal anion was found to be 9.5 charges per 100 carbon atoms. When hexamethylphosphoramide (HMPA) is used as a solvent, an electron transfer agent is not required since alkali metals are soluble in HMPA and can react directly with coal (1).

Alkylation of the Coal Anion and the Effect of Alkyl Groups on the Solubility of the Alkylated Coal. Alkylation of the coal anion by alkyl halide is analogous to that of anthracene anion (equation 5)



(5)

and may be formulated according to equation (6)

$$\text{Coal}^{n-} + nRX \rightarrow \text{Coal } nR + nX^- \qquad (6)$$

where n, the number of negative charges associated with the coal anion expressed in charges per 100 carbon atoms, is about 11. These are the negative centers that are theoretically available for alkylation. The number of alkyl groups actually introduced was 8.1 and 8.8 per 100 carbon atoms in the case of methyl and ethyl, respectively.

A large portion (52%) of the methylated coal is insoluble in benzene in spite of the fact that the number of methyl groups per 100 carbon atoms is almost as high (7.4) in the benzene insoluble as in the benzene soluble portion (8.4).

Table 2 illustrates the effect of alkyl groups on solubility. Ethyl and butyl groups are about twice as effective as the methyl groups in imparting benzene

solubility to the alkylated coal. The ethyl group is almost four times as effective as the methyl group and the butyl group almost twice as effective as the ethyl group in solubilizing coal in hexane.

Molecular Weights and Structure of Alkylated Coal and Petroleum Asphaltenes. The fact that introduction of alkyl groups into lvb coal produces a benzene-soluble material points to a relationship between this type of lvb coal and petroleum asphaltenes. The latter are soluble in benzene in spite of the fact that they contain a larger number of rings (3,4) (8 to 9) per cluster than coal (4) (3 to 4 rings per cluster). However, petroleum asphaltenes, in contrast to coal, contain a considerable number of alkyl groups attached to the aromatic clusters (3). It is these alkyl groups which impart benzene solubility to the petroleum asphaltenes by preventing stacking of the aromatic clusters. The conversion of a lvb coal into a benzene-soluble product by introduction of alkyl groups indicates that the difference between this coal and petroleum asphaltenes is not one of molecular size but one of molecular structure. This view is supported by the fact that the molecular weights of alkylated coal and petroleum asphaltenes are in the same range as may be seen in Table 3. The higher molecular weight of the butylated as compared to the ethylated coal is merely a reflection of the higher molecular weight of the butyl group. On an alkyl-free basis, the difference between the molecular weights is only 7%, i.e., within the limit of experimental error. Hodek (5), who converted coal by acylation into a benzene-soluble product, reported a molecular weight (on acyl-free basis) of about 2000. The molecular weight of 4200 obtained for the petroleum asphaltenes is in good agreement with values reported in the literature (6). Petroleum asphaltenes resemble lvb coal not only with regard to molecular weight but also with regard to chemical reactivity. A petroleum "asphaltene anion," prepared in the same manner as the coal anion, contained 8 negative charges per 100 carbon atoms, i.e., about as much as the corresponding coal anion. Methylation of the asphaltene anion with C-14 labelled methyl iodide yielded a methylated asphaltene containing 5 methyl groups per 100 carbon atoms, i.e., about half as many alkyl groups as were incorporated into the coal molecule. This difference may be due to steric hindrance caused by the presence of alkyl groups in the aromatic clusters of the petroleum asphaltenes.

SUMMARY

Pocahontas (lvb) coal, when treated with alkali metal in tetrahydrofuran in the presence of a small amount of naphthalene, is converted to a "coal anion." The coal anion is formed by transfer of negative charges from the alkali metal to the aromatic clusters in coal with naphthalene acting as an electron transfer agent. The coal anion, containing about 11 charges per 100 carbon atoms is readily alkylated by alkyl halides. The alkylated coals contain about 8.5 alkyl groups per 100 carbon atoms and are soluble in benzene at room temperature. The molecular weight of the alkylated coals is in the same range as that of petroleum asphaltenes. The solubility in benzene of alkylated coal and of petroleum asphaltenes is believed to be due to the presence of alkyl groups which prevent stacking of the aromatic clusters.

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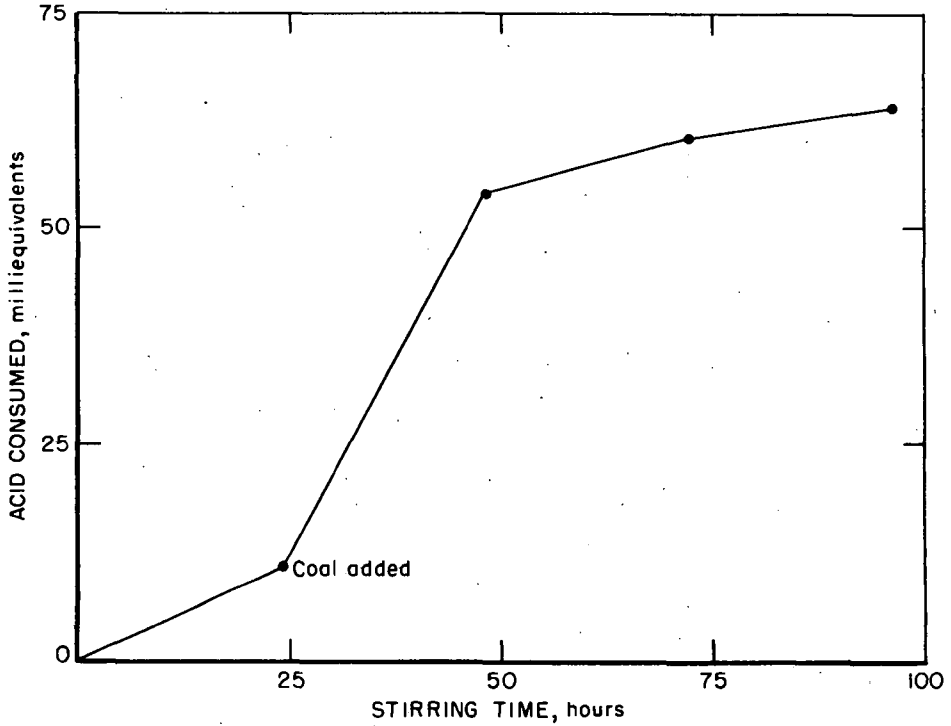

Figure 1-Titration of the coal anion

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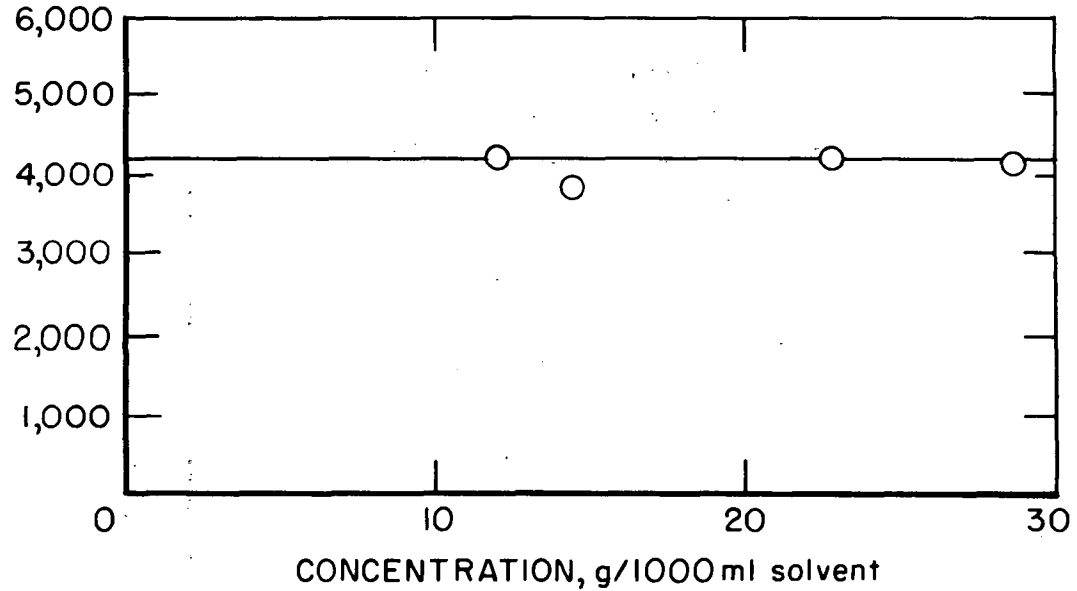

Figure 2 – Concentration dependence of apparent molecular weight by VPO of butylated coal.

L-11493

OXIDATION STUDIES ON COKING COAL RELATED TO WEATHERING

Part II: The Distribution of Absorbed Oxygen in the Products Resulting from the Pyrolysis of Slightly Oxidized Coking Coal

by

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INTRODUCTION

In the previous paper (1) of this series, the reduction of the dilatation of coking coal caused by oxidation in air (2) was studied in connection with the development of a more sensitive and a more generally applicable method of detecting trace oxidation of coal. It was found inter alia, that for Moss 3+ coal, the decrease in dilatation was a very sensitive indicator of the degree of oxidation. The total oxygen content, measured by neutron activation, was 8.55%. A relatively insignificant increase in the oxygen content of this coal by an additional 0.2% to 0.4% caused a decrease of the dilatation from 15% to 25%. The exposure of a minus 20-mesh, fresh sample of this coal for three days in the laboratory, at room temperature caused a marked decrease (5% to 10%) in the dilatation. An increase of the oxygen content in this coal by approximately 1.3%, bringing the total to 9.85%, caused the complete disappearance of both coking and dilatation properties. This level of oxygen content was reached after air oxidation of this coal in an oven at 100°C for 72 hours.

There are some differences of opinion on the subject of the mechanism of the low-temperature oxidation of coal. However, on the basis of a number of papers (3, 4, 5, 6), the conclusions are that low-temperature oxidation from a chemical point of view leads only to:

1. An increase in the reactive oxygen groups (-OH, - COOH, C=O).

2. A small decrease in the aliphatic and alicyclic carbon and hydrogen content of coal.

+ ASTM Classification, high-volatile A bituminous coal, International Classification of Hard Coals 535.

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It was therefore of considerable interest to examine in greater detail the manner in which small changes in the reactive-oxygen groups affect certain physicochemical properties of coking coal, for instance, dilatation. It seemed to us that any light that could be shed on this problem would be of great significance from the point of view of understanding the role of oxygen in the chemistry of the coking process. This investigation was therefore aimed at clarifying certain aspects of this problem.

EXPERIMENTAL

The investigations were conducted mainly on Moss 3 coal, though Itmann coal[++] was occasionally used.

Samples of the fresh coals, which were delivered directly from the mines, were ground in an argon atmosphere to pass the 200-mesh (Tyler) screen. Each was oxidized in the two following ways:

by using atmospheric air, and

by using labelled oxygen (O_2^{18}).

The oxidation by atmospheric oxygen was performed either in an oven (100° for seventy-two hours), or by use of an IR lamp (250W) under the conditions described in a previous paper (1).

Oxidation by labelled oxygen was carried out, as follows:

A 10.5-g portion of Moss 3 coal was placed in a 250-ml Erlenmayer flask. A gas-tight one-way capillary stopcock was then sealed to the top of the flask. The sample was evacuated for three hours at room temperature. Then the temperature was raised to 70°C and the evacuation continued until the inside pressure dropped to 0.2 mm of Hg. At that time, 100 ml of labelled oxygen (99.85% by volume of O_2^{18}) was introduced, followed by an equal volume of argon. The capillary stopcock was closed and the flask was sealed below the stopcock to completely exclude the introduction of atmospheric oxygen. The sealed flask was subsequently placed in an oven at 100°C for seventy-two hours. The concentration of O^{18} in such oxidized coal was 0.66% by weight. The product after oxidizing the coal with O_2^{18} is referred to as oxy-O^{18} coal.

The coal samples, which were oxidized by use of atmospheric oxygen or an IR lamp, were pyrolyzed under vacuum in the manner previously described (1), except that the total time of pyrolysis was increased from ten minutes to fifteen minutes. The pyrolysis experiments were conducted by heating successive samples of coal to successively higher temperatures, at intervals of approximately 50°C, over the range of temperature 350°C to 800°C. The

[++]ASTM Classification, low-volatile bituminous coal, International Classification of Hard Coals 333.

content of carbon dioxide and carbon monoxide was analyzed in the pyrolysis gas evolved up to a given temperature using a Fisher Partitioner with a double-column hexamethylphosphoramide on Chromosorb P, followed by Linde molecular sieve 13X. Helium, with a thermal conductivity detector, was used as the carrier gas at a flow rate of 40 ml/min.

Identical experiments were conducted on samples of fresh unoxidized Moss 3 coal. The results are presented in Figure 1, which shows the difference between fresh and oxidized coal with respect to the oxygen evolved, in the form of CO and CO_2 per gram of coal, as a function of the final temperature of pyrolysis. The pyrolysis of Moss 3 coal, oxidized with $O_2{}^{18}$, was conducted in a manner that excluded oxidation by atmospheric oxygen. After oxidation, the coal samples were transferred to the vacuum-pyrolysis apparatus described previously (1), and pyrolyzed in the temperature range 450° to 950°C. The concentrations of CO^{16}, $CO_2{}^{16}$, CO^{18}, $CO^{16}O^{18}$ and $CO_2{}^{18}$ in the pyrolysis gases were determined by a CEC 21-104 Mass Spectrometer.

The cokes obtained from the pyrolysis of oxy-O^{18} coal under a vacuum at temperatures from 100° to 950° were subjected once more to a pyrolysis process at a temperature of 1050°C. All oxygen-containing gaseous products of pyrolysis were then converted to carbon monoxide by use of a lampblack-nickel catalyst. The pyrolysis and conversion were conducted using the method described previously (7), with the exception that the composition of converted gas was analyzed by mass spectrometer. To obtain the necessary level of accuracy in determining the concentration of CO^{18} and CO^{16}, it was necessary to analyze the content of C_2H_6 and C_2H_4 in the gas samples from the direct pyrolysis of oxy-O^{18} coal. The contents of ethane and ethylene were determined using a chromatograph (Aerograph 1500 equipped with a flame-ionization detector and a copper column, 0.25-inch ID by 30 feet length and one-quarter inch diameter, packed with silicone DC 200 on Chromosorb P). The flow rate of nitrogen used was 33 ml/min.

RESULTS AND DISCUSSION

Interesting information can be derived from Figure 1, concerning the influences of the two methods of oxidizing coal (IR lamp or oven at 100°C) on the differences in yield of oxygen, in the form of CO_2 and CO, in the resulting gaseous products from the pyrolysis of the oxidized coal (oxycoal). The conditions were selected so that the amount of oxygen absorbed by each coal during oxidation was the same for both methods of oxidation. At a given temperature of pyrolysis, more oxygen in the form of CO_2 and CO was evolved per gram of coal when samples were subjected to photo-oxidation under the IR lamp than if they were oxidized in the oven. For the samples photo-oxidized by IR lamp, the temperatures of pyrolysis for which $O_2 = O_2\,(CO_2 + CO)_{oxid} - O_2\,(CO_2 + CO)_{fresh}$ = a constant are relatively clear, and can be determined as 650°C for Itmann coal and 752°C for Moss coal. A similar plateau cannot be

found in the case of the oxidation of the coals in air in an oven at 100°C. It will also be observed that the amount of oxygen evolved in the form of CO_2 and CO during pyrolysis of the samples, oxidized at 100°C, was much lower than that when oxidation was conducted by use of an IR lamp. A possible explanation of this is that a considerable amount of oxygen absorbed by coal oxidized during the process of oxidation at 100°C, was later evolved in the form of water or linked with the tar during the subsequent pyrolysis of this oxycoal. The shapes of the appropriate curves in Figure 1 suggests this possibility.

The investigations to follow were limited to Moss 3 coal which was selected for the ease with which this coal oxidizes and for its fluid character. Labelled oxygen, O_2^{18}, was used for the oxidation of this coal at 100°C, as previously described. It was assumed that the mechanism of the oxidation of Moss 3 coal at 100°C would resemble a somewhat accelerated weathering process. The advantages of this method of oxidation were that even though the coal was but slightly oxidized, similar to weathered coal, it was still possible to identify and determine, with precision, the low concentrations of products, such as, CO^{18}, CO_2^{18}, $CO^{18}O^{16}$ and H_2O^{18}. The results obtained directly from pyrolysis of oxy-O^{18} coal are presented in Table I. These data are presented graphically in Figure 2 to show the different manner in which the gases are evolved. The amount of O^{18} in the form of CO_2^{18} and $CO^{18}O^{16}$ in gas from pyrolysis reaches the highest value at 450°C and remains on the same level during successive pyrolysis experiments at higher temperatures, right up to 950°C. The manner in which the CO_2^{18} and $CO^{18}O^{16}$ are evolved during pyrolysis of oxy-O^{18} coal seems to be strong evidence that some oxygen groups, created during oxidation of this coal, decompose completely to CO_2^{18} or $CO^{18}O^{16}$ below 450°C.

The continuous increase of O^{18} evolved in the form of CO^{18} may be observed in Figure 2, during the increase of the temperature of pyrolysis. The shape of the curve of evolution of O^{18} in the form of CO^{18} is similar to the analogous curve for CO^{16}. However, even here, especially at lower temperatures of pyrolysis, the relative amount of evolved CO^{18} is much higher than for CO^{16}.

The relatively high concentration of combined O^{18} in the gaseous products of low-temperature pyrolysis agrees with the independently measured rapid decrease of O^{18} in the resulting coke, as shown in Figure 3. About 60% by weight of O^{18} present in oxy-O^{18} coal is removed during pyrolysis of this coal at 400°C. Only about 14% of O^{16} is removed from the same coal during pyrolysis at 400°C. It will also be observed in Figure 3 that when the pyrolysis temperature reached 430°C, which is the temperature of maximum contraction of Moss 3 coal, a rapid decrease in the concentration of O^{18} and O^{16} in semi-coke occurred.

The evidence from the pyrolysis of oxy-O^{18} coal, presented in Figure 4, showed that the main part of O^{18} occurs in the pyrolysis product we may call

"tar + water". The data presented in this figure were obtained from a material balance derived from the results previously presented in Tables 1 and 2. This material balance was based on the quantity of coke and gas produced per gram of coal, the experimental concentrations of O^{18} in the coke and gas, and the measured initial amount of O^{18} in oxy-O^{18} coal before pyrolysis. The determination of O^{18} in the coke and gas requires some additional comment. For the determination of O^{18} in coke, the method described in the earlier paper (8) was applied, with the exception that the concentration of CO^{18} in converted gas was determined by mass spectrometry on the basis of the peak at $\frac{m}{e}$ 30. The concentration of C_2H_6, in the converted gas, was found by gas chromatography to be less than 10^{-3}% by volume. So, the interference by this constituent at $\frac{m}{e}$ 30 should not be a serious matter. When the concentrations of CO^{18} and CO^{16} in gas from direct pyrolysis of oxy-O^{18} coal were determined, the concentrations of C_2H_6 were measured in the gas samples from each pyrolysis experiment by gas chromatography.

The results obtained were taken into account to find the proper concentrations of CO^{18} from mass spectrum. From the precautions taken and the level of reproducibility, it was considered that the concentrations of O^{18} found in coke and gas, as shown in Figure 4, were characterized by a relatively high level of accuracy. Therefore, the calculated concentration of O^{18} in tar + water owing to its relative magnitude, should likewise have comparable accuracy. It is necessary to stress the importance of this accuracy, due to the significance attached to the oxygen present in the tar in determining the coking properties of coal, and due to the surprisingly high concentration of O^{18} in tar + water obtained from pyrolysis at 450°C. This amounts to a concentration of O^{18} in the tar + water of about 3.8% to 4.0% by weight. In spite of the fact that the tar + water consisted only of about 10% by weight of oxy-O^{18} coal, it contained approximately 60% of all O^{18} absorbed by this coal during oxidation. On the other hand, the concentration of O^{18} in the semicoke from pyrolysis at 450°C is relatively small, that is, 15% of the labelled oxygen existing in oxy-O^{18} coal, which is approximately 0.08% to 0.1% by weight of coke.

The observation that the highest concentration of O^{18} was found in the part of the organic matter of coal, which cracks to produce tar + water during low-temperature pyrolysis, appears to be consistent with the view that this part of the oeganic matter of coal can be roughly identified with the most extractable part of coal. This fraction, in the opinion of many authors, is responsible for coking properties (8,9).

Removacek (9) has found that the oxidation of coking coal can cause the change of the chemical character of its chloroform extract, which becomes similar to the chloroform extract from non-coking coals. In this paper, by quite a different route, it has been found that relatively slight oxidation of coal causes the largest changes, measured by increase of oxygen, in the part of the coking coal, which can most easily be cracked during heating to form tar.

It seems highly unlikely that the mild conditions of oxidation applied in this research could basically change the structure of the tar portion of this coal other than that a number of reactive-oxygen groups were introduced. Berkowitz (8) suggests that the oxygen in the form of COOH or OH groups cannot cause the change of coking properties of coal. Though a slight increase of these groups, during oxidation of coal, can probably not bring about - by itself - so marked a change in the physico-chemical properties of coal; nevertheless, there appears to be a strong possibility that the thermal decomposition of the OH groups, created during oxidation, results in the formation of ether-type crosslinks of very considerable thermal stability. A very small number of such bonds can stiffen the whole structure, and decrease the plastic properties of coal, especially the dilatation. The tar fraction is of special significance as a potential source of ether bonds, because of the high content of oxygen shown to be introduced into this fraction. Creation of crosslink ether bonds should be accompanied by the evolution of water, in our case, H_2O^{18}. It was found by mass spectrometry that the ratio H_2O^{18}/H_2O^{16} possessed the highest value when the pyrolysis experiments were conducted at the lowest temperatures, Table 3. Mass spectrometry also revealed that approximately 0.5 ml of H_2O^{18} (in gaseous state; 760 mm of Hg; 20°C) was evolved during pyrolysis of oxy-O^{18} coal. Since there exists the same probability of evolution of H_2O^{18} as H_2O^{16} as the result of the condensation of such groups as R_1 - $O^{16}H$ and HO^{18} - R_2, this means that the volume of gaseous water at 760 mm of Hg and 20°C evolved from condensation reactions leading to the disappearance of dilatation properties will be approximately one ml. It can be concluded from this observation that only about 12% of the total labelled oxygen absorbed during oxidation is responsible for the loss of dilatation resulting from the ether bonds. It should be mentioned that the proportionate increase of non-reactive oxygen groups (ether groups) in cokes, that occurs on low-temperature pyrolysis has been noted by other scientists (10,11). This seems to be substantial, though not sufficient confirmation of our hypothesis that it is not the OH groups per se that cause the loss of swelling properties but the fact that these groups undergo condensation reactions as the temperature is elevated to yield ether type cross links. The search for additional support for this hypothesis will be the purpose of the next paper of this series.

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Table 1. Per cent by volume of CO^{16}, CO^{18}, $CO_2{}^{16}$, $CO^{16}O^{18}$, and $CO_2{}^{18}$ in gas from the direct pyrolysis, at different temperatures, of Moss 3 coal oxygenated with $O_2{}^{18}$.

Temperature of Pyrolysis (°C)	% By Volume					Total Gas ml/g
	CO^{16}	CO^{18}	$CO_2{}^{16}$	$CO^{16}O^{18}$	$CO_2{}^{18}$	
450	4.7	1.71	5.6	3.45	1.72	23.2
500	3.9	1.04	4.1	1.62	0.81	49.2
550	5.4	0.92	3.0	1.08	0.54	74.0
600	5.1	0.73	2.4	0.76	0.38	105.0
650	5.0	0.64	2.1	0.61	0.30	132.0
700	6.5	0.51	1.8	0.48	0.24	168.0
750	6.4	0.47	1.6	0.40	0.20	201.0
800	6.9	0.52	1.4	0.35	0.17	229.0
850	7.2	0.44	1.2	0.29	0.14	280.0
900	9.1	0.55	1.1	0.24	0.12	329.0
950	9.4	0.50	1.1	0.23	0.11	354.0

Table 2. The composition of gas from pyrolysis and conversion process (1050°C) of cokes obtained from Moss 3 coal oxygenated with O_2^{18} and pyrolyzed at indicated temperatures.

Temperature of Pyrolysis (°C)	% By Volume						Total Gas ml/g
	CO^{16}	CO^{18}	$CO_2{}^{16}$	H_2	CH_4	H_2S	
70	17.4	1.16	0.01	81.0	0.14	0.00	712.0
350	17.3	0.68	0.03	81.4	0.19	0.00	661.6
400	16.5	0.51	0.10	82.7	0.15	0.00	640.7
450	14.5	0.27	0.00	84.9	0.15	0.21	478.2
500	15.1	0.18	0.00	84.5	0.15	0.02	413.1
550	15.9	0.13	0.12	82.6	1.10	0.10	382.1
600	17.7	0.11	0.10	81.3	0.50	0.25	332.9
650	18.2	0.11	0.12	81.3	0.14	0.10	283.1
700	19.7	0.08	0.00	81.3	0.11	0.11	224.7
750	24.1	0.08	0.10	75.1	0.05	0.11	171.7
800	21.5	0.05	0.16	78.0	0.00	0.09	137.8
850	25.3	0.07	0.10	74.5	0.00	0.07	104.4
900	27.4	0.06	0.09	71.8	0.00	0.00	70.9
950	31.4	0.04	0.01	68.2	0.03	0.00	46.5

Table 3. The percentage of H_2O^{18} in totally evolved water.

Temperature of Pyrolysis (°C)	% By Volume H_2O^{18}
450	12.4
500	11.2
550	8.3
600	6.0
650	6.4
700	6.0
750	5.9
800	5.4
850	4.9
900	4.9
950	3.6

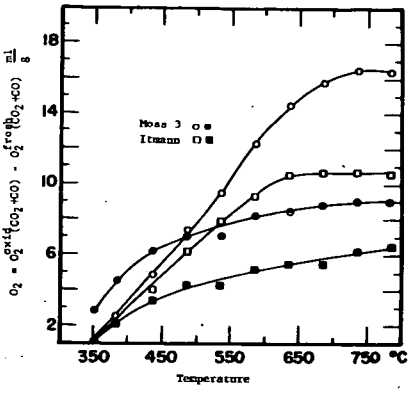

FIG. 1 The difference in the evolution of CO_2 and CO expressed as O_2 from fresh and oxidized coal as a function of the temperature of pyrolysis.

o□ 15 min. IR and air

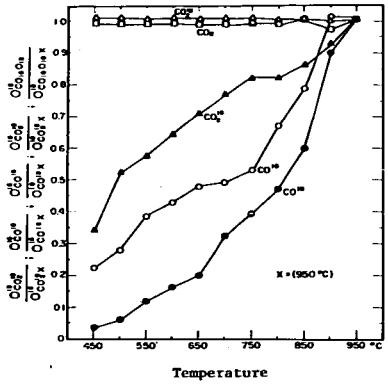

FIG. 2 The evolution of O^{18} and O^{16} in form of gaseous products of pyrolysis compared to amount of these products evolved at temperature 950°C.

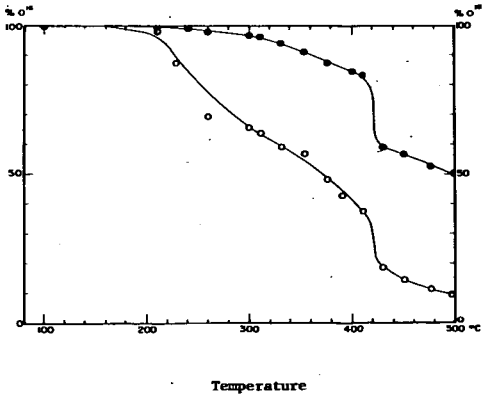

FIG. 3 Decline of the content of O^{18} and O^{16} in semicokes obtained during heating at indicated temperatures Moss 3 coal oxidized with labeled oxygen.

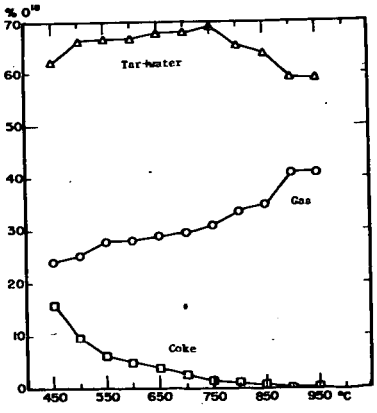

FIG. 4 Distribution of O^{18} in pyrolysis products of Moss 3 coal oxidized with labeled oxygen.

SOLVATION OF SOME BITUMINOUS COALS IN QUINOLINE BY ULTRASONIC IRRADIATION

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INTRODUCTION

The first application of ultrasonic irradiation to disperse the α fraction of coal in pyridine was reported by Berkowitz.[1] Kirkby, Lakey, and Sarjant have investigated the ultrasonic solvation of coals of different ranks in pyridine.[2] In addition to an infrared study of the coal extracts, these authors have described the effects of irradiation time, coal rank, particle size, and charring temperature on the amount of coal solubilized. Littlewood, who also used pyridine as a solvent, studied the solubilization of coal as a function of the distance of the extraction vessel to the ultrasonic transducer, generator output power, and coal rank.[3] We have described the ultrasonic solvation of hvab coal at ambient temperature using quinoline, pyridine, formamide, N-N-dimethylformamide, and 1,2,3,4-tetrahydronaphthalene as solvents.[4] In our investigation the highest yield of extract was obtained with quinoline; after 4 hours of ultrasonic irradiation approximately half of the coal was solubilized, two and one-half times the yield with pyridine.

EXPERIMENTAL

The identification of the coals used in this investigation are given in table 1.

Table 1.- Identification of coals

Coal	Identification
1	Vitrain, high-volatile A bituminous Pittsburgh seam, Bruceton, Allegheny County, Pennsylvania
2	High-volatile A bituminous, Pittsburgh seam, Valley Camp No. 3, Ohio County, West Virginia
3	High-volatile A bituminous, bottom bench, Noon Mine, Ohio
4	High-volatile A bituminous, Kentucky No. 11 bed, Vogue Mine, Muhlenberg County, Kentucky
5	High-volatile B bituminous, Illinois No. 5 (c) Red Ember No. 2, Fulton County, Illinois

A commercial ultrasonic generator operating at a frequency of 80 Khz with a total power output of 80 watts was used. Samples of coal in 5 ml of solvent were ultrasonically irradiated at ambient temperature in an air atmosphere. The irradiation time used is given in each experiment. The coal-quinoline slurries were irradiated in flat bottomed glass vials (80 mm x 20 mm diameter). The vials were immersed in the ultrasonic generator tank (containing H_2O) to the position at which maximum agitation of the sample was observed. After irradiation, the solvent-extract mixture was removed from the coal residue by centrifugation. The

coal residue was then washed with two 5-ml portions of quinoline and two 5-ml portions of benzene. The residue was then air dried at 100° C to constant weight and used as the basis for determining the amount of solvation according to the method of Curran and co-workers;[5] the yields of extract determined by this method are on a maf basis.

RESULTS AND DISCUSSION OF RESULTS

Parameter Investigation

Carbon Content

One-half gram samples of various coals (-325 mesh) and 5 ml of quinoline were ultrasonically irradiated for 4 hours at ambient temperature. The results are given in table 2.

Table 2.- Amount of coal solvated versus carbon content

Sample	Rank	Weight percent solvated	Carbon content of starting coal, percent (maf)
Coal 1*	hvab	49.2	82.9
2	hvab	23.2	81.7
4	hvab	17.8	78.8
5	hvbb	17.6	76.9

* See table 1 for complete identification of samples

These data show that a correlation exists between carbon content and the amount of coal extracted with quinoline. Of the coals investigated, the amount of material solubilized decreased as the carbon content of the starting coal decreased. Kirkby and co-workers reported a definite relationship between carbon content and the amount of coal solubilized by pyridine.[2]

Irradiation Time--Coal

One-half gram samples of Pittsburgh seam hvab vitrain (-325 mesh) and 5.0 ml of quinoline were ultrasonically irradiated for periods ranging from 15 minutes to 24 hours at ambient temperature. A control was obtained by adding coal to the quinoline and then immediately removing the solvent using the standard procedure described earlier. The results are shown in figure 1. The amount of coal solvated varied from 16 percent for 15 minutes of irradiation to 77 percent for 24 hours. The largest increase in solubilized material occurred during the first 2 hours of irradiation. Littlewood has reported that the highest extraction rate for Brockwell 301 coal in pyridine occurred during the first hour of irradiation.[3]

Coal Chars

The chars used in these experiments were prepared by the following procedure: Pittsburgh seam hvab coal was heated to the desired temperature for 1 hour in a nitrogen atmosphere, air cooled, and then crushed to size. Chars were produced at temperatures of 275° C, 375° C, and 475° C. One-half gram samples of the starting coal (30 x 80 mesh) or char (30 x 80 mesh) were added to 5 ml of quinoline and ultrasonically irradiated for 4 hours. The results are shown in table 3.

Table 3.- Solvation as a function of charring temperature

Char	Weight percent solvated
Starting coal	18
275° C	6
375° C	37
475° C	17

Solvation of similar chars has been described by Walters and co-workers using Soxhlet extraction with chloroform as the solvent.[6] Chloroform solubilities of 0.6, 4.8, and 1.1 percent were reported for 300° C, 400° C, and 500° C chars, respectively. In both the ultrasonic and Soxhlet extractions, yields followed the same pattern. Walters has also concluded that maximum extraction occurs for chars prepared at the temperature of maximum fluidity. In contrast to this, Kirkby and co-workers reported that, for a vitrain-pyridine mixture, greatest ultrasonic solvation occurred with the original coal.[2]

Particle Size

A portion of the 375° C char (30 x 80 mesh) used in the experiments described previously was crushed to -325 mesh. One-half gram samples of the 30 x 80 mesh or -325 mesh chars and 5 ml of quinoline were ultrasonically irradiated for 4 and 24 hours. The results are shown in table 4.

Table 4.- Solvation versus particle size

Irradiation time (hours)	Mesh size	Weight percent solvated
4	-325	65
4	30 x 80	37
24	-325	82
24	30 x 80	77

For the shorter irradiation time, these data show that the particle size of the starting coal is an important factor for the ultrasonic solubilization of chars in quinoline. After extensive irradiation (24 hours) both sizes of char produced approximately the same amount of solvate. Littlewood, using coal-pyridine systems, has also reported that the amount of ultrasonic solubilization is dependent upon the particle size of the starting material.[3]

Irradiation Time--Char

Figure 1 also shows the percent solvation in quinoline versus irradiation time for a 375° C char (-325 mesh) produced from Pittsburgh seam coal. The amount of char solvated ranged from 46 percent for 2 hours to 82 percent for 24 hours. The solvation rate for the char is similar to that of the vitrain, the highest extraction rate occurring during the first 2 hours of irradiation for both materials.

Temperature

Ten percent slurries of Pittsburgh seam hvab coal (-325 mesh) in quinoline were ultrasonically irradiated for 4 hours at ambient temperature and 80° C. The results of these experiments are given in table 5.

Table 5.- Coal solvation as a function of temperature

Temperature	Weight percent solvated
Ambient (36° C)*	22
80° C	25

*Ultrasonic action increased the temperature of the water bath to 36° C

Littlewood found that extraction at 90° C did not increase the yield of solubilized coal in pyridine.[3] Littlewood also stated that this was contrary to the findings of Mertins, who reported that a temperature of 80° C gave a three-fold increase in solvation yield.[7] Our data appear to substantiate the findings of Littlewood; namely, a two-fold increase in temperature relative to ambient temperature has little effect on ultrasonic solubilization.

Sulfur Removal

One-half gram samples of various bituminous coals (-325 mesh) in quinoline were ultrasonically irradiated for 4 hours at ambient temperature. Total sulfur analyses were obtained for the extracts. The results of these analyses and the analyses of the starting coals are shown in table 6.

Table 6.- Sulfur analyses

Sample	Rank	Weight percent sulfur		Percent removed
		Extract	Starting coal	
Coal 1*	hvab	0.6	1.0	40
2	hvab	1.9	3.5	46
3	hvab	4.1	7.5	46
5	hvbb	2.1	3.9	45
375° C char, Pittsburgh seam coal		0.7	1.2	42

* See table 1 for complete identification of samples.

In these five samples the sulfur is 40 to 46 percent lower in the extracts than in the starting coal.

To determine the type of sulfur removed by ultrasonic solubilization of coal, sulfur forms analyses were obtained from a quinoline extract of a Kentucky No. 11 raw head coal sample. See Coal 4, Table 1, for complete identification of sample. The results of the extract together with data for the starting coal are given in table 7.

Table 7.- Sulfur forms analyses

	Weight percent			
	Total S	Pyrite S	Organic S	Sulfate S
Starting coal	5.5	3.7	1.8	0.12
Extract	1.9	0.03	1.8	0.04

These data show that removal of the pyritic sulfur accounts for the decrease in sulfur content of the extract.

Ash Removal

Ash determinations were made on the extracts prepared as described above. The results, together with the analyses of the starting coals, are given in table 8.

Table 8.- Ash analyses

Sample	Rank	Weight percent		Percent removed
		Extract	Starting coal	
Coal 1*	hvab	1.3	1.7	24
2	hvab	1.0	6.7	85
3	hvab	3.4	15.4	78
4	hvab	3.3	12.4	87
375° C char, Pittsburgh seam hvab		1.0	7.5	73

* See table 1 for sample identification

The lower ash values in the quinoline extracts can be attributed to ultrasonic grinding which causes submicron size particles to be formed; the ash particles are removed from the extracts by a washing procedure during the extract preparation described earlier. Evidence for this phenomenon was observed in the following experiment. The wash water from one of the extract preparations was saved and evaporated to dryness. The fluffy light-brown residue that remained was analyzed by emission spectroscopy and found to contain 20-30 percent Si, 10-20 percent Al, and 1-5 percent Fe. The concentrations of Si, Al, and Fe are similar to those found in coal ash.

Reuse of Quinoline

It has been observed in an investigation utilizing a high-boiling coal-tar fraction as a solvent that the solvating power of the recycle material decreased by several percent with each pass.8/ In order to determine if high molecular weight compounds produced by the sonolysis of quinoline or extracted during the

ultrasonic irradiation of coal-quinoline mixtures affect the efficiency of recycled quinoline, the following experiments were performed.

The fresh quinoline used in this investigation has a boiling range of 235°-237° C and contains approximately 0.1 percent methyl quinolines as determined by mass spectrometry. The distillate of the solvent from ultrasonically irradiated quinoline-coal extract mixtures contains a fraction boiling from 235°-239° C (primarily quinoline), Fraction 1, and a fraction boiling higher than 239° C, Fraction 2. Fraction 1 constitutes 98 percent of the distillable solvent and Fraction 2 constitutes the other 2 percent. The doped solvent used in this experiment consisted of 90 percent of Fraction 1 (b.p. 235°-239° C) and 10 percent of Fraction 2; the concentration of higher boiling material was, therefore, 5 times more than that found in ultrasonically irradiated quinoline-coal mixtures.

One-half gram samples of Pittsburgh seam hvab coal (-325 mesh) and 5 ml of doped quinoline or Fraction 1 (see above) were ultrasonically irradiated for 4 hours at ambient temperature. The results of these experiments, and of an extraction with "fresh" quinoline, are shown in table 9.

Table 9.- Solvation of coal in used quinoline

Solvent	Weight percent of coal solvated
Doped-reclaimed quinoline (10 percent boiling > 239° C)*	28
Fraction 1 (b.p. 235°-239° C)*	29
"Fresh" quinoline (b.p. 235°-237° C)	27

* See text for description

In another series of experiments, slurries consisting of 0.5 gm Pittsburgh seam hvab coal (-325 mesh) and 5.0 ml of solvent were ultrasonically irradiated for 4 hours at ambient temperature. After the coal residue was removed following each extraction, the quinoline and extracted material were used as the "solvent" for the next extraction of "fresh" coal. The results of these experiments are shown in table 10.

Table 10.- Recycled quinoline extract and fresh coal

Experiment	Solvent	Cumulative extract, weight percent	Weight percent solvated in 4 hours
I*	Fresh quinoline	26	26
II	Quinoline + extract from I**	52	26
III	Quinoline + extract from II**	88	28
IV	Quinoline + extract from III**	-	Not obtained, see text

* 0.5 gm Pittsburgh seam hvab coal (-325 mesh) used for all 4 experiments.

** Solvent (quinoline + extract) obtained from preceding experiment by removal of coal residue by centrifugation.

The mixture at the end of Experiment IV was so viscous that it could not be separated by centrifugation. Consequently, the percent of coal solvated could not be determined.

From these data it appears that high-boiling compounds extracted (or produced by the sonolysis of the solvent) during the ultrasonic irradiation of coal-quinoline slurries have little or no effect on the amount of coal solubilized by reused quinoline.

Crude Quinoline-Base Mixture

A 0.5 gm sample of Pittsburgh seam hvab vitrain (-325 mesh) and 5 ml of crude quinoline bases were ultrasonically irradiated for 4 hours at ambient temperature. The crude quinoline bases (obtained from a commercial high-temperature coking operation) had a boiling range of 99° C to 238° C and contained 50 percent quinoline. Only one percent of the coal was solubilized.

The crude quinoline-base fraction was found to contain 9 percent H_2O. To determine if H_2O inhibits ultrasonic extraction, 0.5 gm of the Pittsburgh seam vitrain (325 mesh) used above and 5.0 ml of a mixture containing 80 percent pure quinoline and 20 percent H_2O was irradiated for 4 hours. This experiment produced only 9.5 percent extract, compared with 49 percent using pure quinoline.

Water was distilled from the crude quinoline-base fraction, and the experiment was repeated. The water-free fraction (boiling range 220°-238° C) solvated 38 percent of the coal. These data indicate that the presence of water reduces the solvation power of the quinoline. Mertins also reported that the presence of water in pyridine reduced the extraction efficiency of the solvent.[7]

SUMMARY

This investigation of the ultrasonic irradiation of bituminous coal-quinoline mixtures has shown:

1. There is an apparent correlation between the carbon content of the bituminous coals investigated and the amount of material solubilized; that is, the amount of material solubilized decreased as the carbon content of the starting coal decreased.

2. The solvation rate for vitrain in quinoline is greatest during the first 2 hours of irradiation

3. A greater yield of extract can be obtained by first charring the coal at the temperature producing maximum fluidity

4. For shorter irradiation times the particle size of the starting coal is an important factor for increased solubilization

5. Increasing the temperature from 36° C to 80° C does not affect the yield of extract

6. The presence of water in quinoline reduces the extraction efficiency of the solvent

7. The solvates produced show marked decreases in sulfur content compared to the starting coal. The decrease in sulfur in the extracts is caused by removal of pyritic sulfur

8. There is a decrease in the ash content of the extracts.

9. Quinoline can be reused as a solvent with no impairment of solubilizing efficiency.

ACKNOWLEDGMENTS

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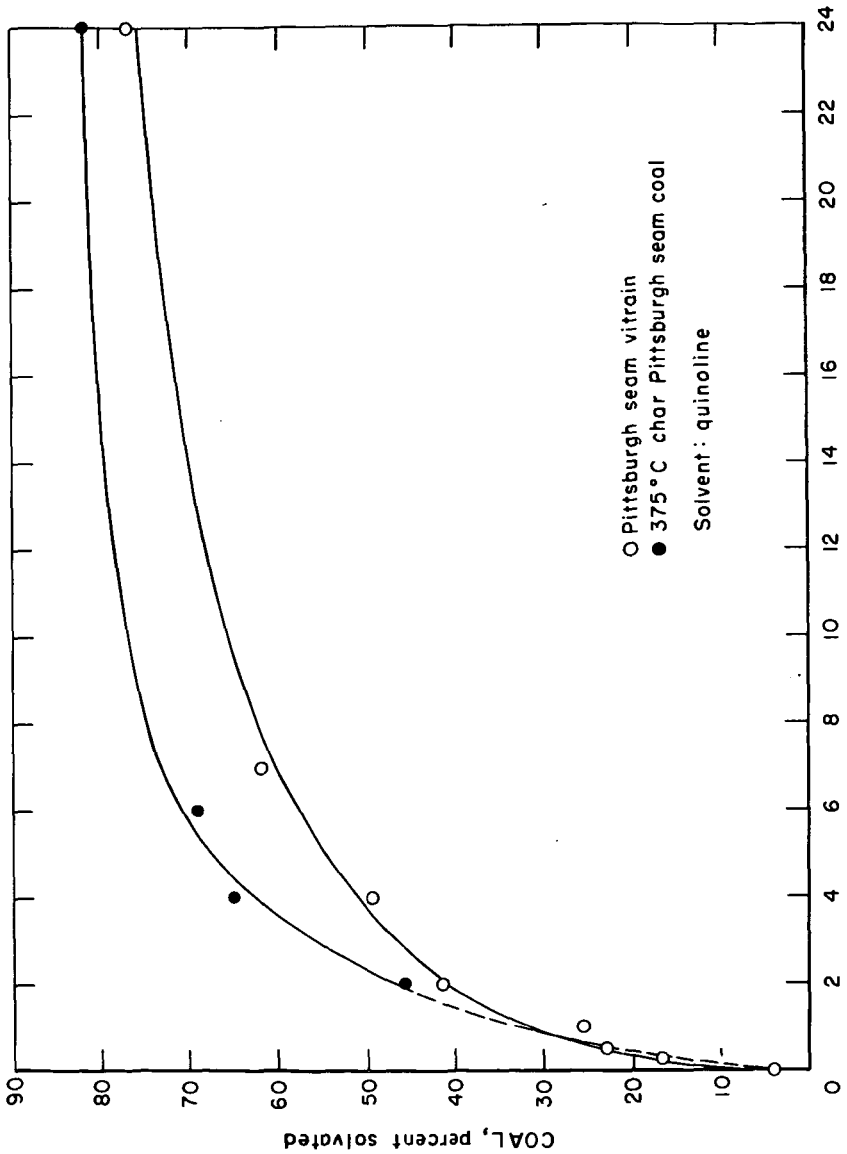

Figure 1.- Percent hvab vitrain and char solvated versus ultrasonic irradiation time.

ULTRASONIC ENERGY EFFECTS ON COAL EXTRACTION BY A HYDROGEN DONOR SOLVENT

by

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ABSTRACT

The kinetics of a high volatile bituminous coal extracted with 1,2,3,4-tetrahydronaphthalene (tetralin) under the influence of ultrasonic energy has been studied.

The extraction of coal has been carried out at five different temperatures: 47°, 57°, 67°, 77°, and 87°C. Effects of intensity of ultrasonic energy, particle size, and hydrogen content of the coal were also obtained.

Analysis of the data showed that a second order rate reaction followed by a first order rate reaction describes the kinetics of the extraction process.

The enthalpies of the second-order and first-order regions were 8.70 K cal/mole and 2.5 K cal/mole, respectively, which suggests that the extraction process is under essentially physical control. Auxiliary experiments and the kinetic data obtained suggest a model for the extraction process. The mechanism of the overall reaction is undoubtedly complex but the data indicate that weak van der Waals and hydrogen bonding forces are most affected by the ultrasonic energy.

INTRODUCTION

The dissolving of coal in solvents has been studied from many aspects. Since the first systematic experiments by De Marsily in 1860[1] many investigators have extracted coal with a variety of organic liquids.

The work carried out before 1950 has been ably reviewed by Dryden[2]. The first experiments using ultrasonic energy were conducted by Berkowitz[3] with some later similar experiments by Littlewood[4]. The influence of solvent properties, experimental conditions and coal types on the yield of extractable material from coal has also been reviewed by Dryden[5]. Very little data have been reported on the kinetics of the extraction process[6]. The influence of ultrasonic energy on the kinetics has also received little attention. Undoubtedly the overall extraction is the result of several types of simultaneous and consecutive reactions due to the complexity of the coal structure involved. However, the results of this study are extremely interesting and, perhaps, can help one to understand the particular effects of ultrasonic waves on the extraction process.

From previous work on coal extraction in the presence of ultrasonic energy the following general conclusions can be drawn:

The amount of material extracted can be significantly increased by the use of ultrasonic energy[3,7,8].

The total amount extracted is dependent upon the temperature of the extraction[6].

The rate of extraction was highest with coal of the smallest particle size[7].

In this study these conclusions were verified for the coal-tetralin system and some further results were obtained leading to other conclusions regarding the mechanism of the reactions taking place.

MATERIALS AND PROCEDURE

The coal used for this study was from the Spring Canyon Coal Mine, Carbon County, Utah. An analysis is given in Table I. The tetralin used was reagent grade.

TABLE I

ANALYSIS OF SPRING CANYON COAL

(Commercial Testing and Engineering Company)

Dry Ultimate	Weight %	Dry Proximate	Weight %
Carbon	72.88	Ash	8.4
Hydrogen	5.58		
Nitrogen	1.51	Volatile Matter	45.70
Oxygen	10.82	Fixed Carbon	45.90
Sulfur	0.62		
Chlorine	0.119		

Dry Heating Value - 13,240 Btu/lb.

The following procedure was followed in the extraction of Spring Canyon Coal:

The coal was ground and sized to -200+270 Tyler mesh. A portion of the ground coal was removed from stock bottle and put in a beaker. The sample was then dried in a vacuum oven at 110°C for a period of four hours, removed from oven, and then placed in a desicator.

The extraction apparatus used for the experiments was a commercial ultrasonic cleaner which generated waves with a frequency of 25 kc/second. The maximum power output was 300 watts. The ultrasonic energy was directed to a stainless steel tank with a surface area of 80 square inches. Figure 1 is a schematic drawing of the extraction apparatus. A measured

volume of solvent was introduced inside the stainless steel tank and heated. When the selected operating temperature was reached, a weighed amount of coal (solvent to coal ratio = 50 ml/1 gram for tetralin and coal and 60/1 for ethylene diamine and coal) was introduced into the tank and mixed with the solvent; then mechanical stirring started. Stirring assured the uniformity of coal-solvent mixture and eliminated the precipitation of coal. Reaction time = zero for each experiment was taken as the time when the coal was added to the heated solvent. Samples were drawn into glass flasks after 5, 10, 20, 30, 40, 50, 60, 90 . . . 540 minutes. The samples were cooled to room temperature and weighed.

Each sample was then placed in a weighed, double thickness Soxhlet extraction thimble. The thimble containing the sample was placed in the Soxhlet extraction tube and was washed with acetone for 24 hours. The thimble containing the coal residue was dried in a vacuum oven at 110°C for 4 hours. The paper thimble and coal residue was then weighed. The weight of the coal residue or that which was not extracted was found by subtraction.

PRELIMINARY EXPERIMENTS

In order to determine some specific effects of operating conditions several preliminary experiments were conducted. These included the following with the results as indicated.

Decomposition of tetralin: Since it has been shown that ultrasonic energy can cause molecular fragmentation of organic liquids[9,10] and also degradation of mixtures and organic solvents in the presence of water[10] some experiments were carried out to determine the effects upon tetralin under the extraction conditions to be used for coal.

Tetralin was analyzed by gas chromatography to determine the quantities of other species present (Figure 2). Next tetralin was irradiated for 24 hours in the tank to be used for extraction with ultrasonic waves (3.75 watts/in^2) at 87°C. Samples of the tetralin were taken during the experiment and analyzed. No detectable decomposition was observed for the first 15 hours; the total decomposition after 24 hours was less than 1.0 per cent. Figure 3 is a chromatogram of the irradiated tetralin.

Coal-Solvent Ratio: In order to be sure that neither the rate nor the extent of extraction would be limited by the amount of solvent present for the coal sample some experiments were conducted to determine the amount extracted by various coal/solvent ratio. Figure 4 shows that for a coal/solvent ratio of 1 gram coal/30 ml of solvent or lower the per cent extracted is essentially constant. For subsequent experiments a ratio of 1 gram coal/50 ml solvent was used.

Particle Size: The effect of particle size on the per cent extracted at a particular temperature was found to be negligible. However, as shown in Figure 5 the initial rate of extraction was higher for the coal with a smaller particle size.

Intensity of Ultrasonic Energy: The ultrasonic generator and power control unit was equipped with facility for controlling the mechanical energy to the tank where the experiments were conducted. As shown in Figure 6 the amount extracted was a function of the ultrasonic energy supplied to the system. For all of the experiments conducted after these preliminary tests 100% of the energy available (3.75 watts/in^2) was used.

Some of the coal used in the experiments was reduced with Lithium-ethylenediamine. Calculations indicated an addition of 12.6 hydrogen

atoms per 100 carbon atoms in the coal. Both raw coal and the reduced coal was extracted with tetralin in the presence of ultrasonic energy. As shown in Figure 7 both the amount extracted and the rate of extraction were greater for the reduced coal.

Stirring Effect: Final preliminary experiments were conducted to determine the effects of stirring on the extraction of coal in the system used. Figures 8 and 9 show comparative data for static extraction, stirred extraction and extraction with stirring and ultrasonic energy at 47° and 87°C. Stirring appears to be important in making fresh solvent available to the coal surface.

RESULTS AND DISCUSSION

Conclusions regarding the effects of ultrasonic energy on the extraction rate and yield referred to previously were confirmed. Figure 10 shows kinetic data obtained in experiments with and without the influence of ultrasonic energy.

It was found that most of the data could be fit very well to a second order equation of the form:

$$\frac{dx}{dt} = k_2 (a-x)^2 \qquad (1)$$

where k_2 = reaction rate constant

a = maximum fraction of the coal which would dissolve at the temperature studied

x = fraction of the coal extracted after any reaction time, t

Integration of the above equation with the lower limit of $x = 0$ when $t = 0$ leads to:

$$\frac{x}{a(a-x)} = k_2 t \qquad (2)$$

A plot of $\frac{x}{a(a-x)}$ versus t should yield straight lines with the slope k_2 for each temperature if equation (1) adequately describes the reaction kinetics. Figure 11 shows the second order plot to be in agreement with the above conditions.

The second order equation was very adequate to describe the first hour of reaction at each of the temperatures studied from 47° to 87°C. However, after 60 minutes the data no longer fit the second order curves. Table II shows the extent of the second order reaction at the temperatures studied.

TABLE II

EXTENT OF SECOND ORDER REACTION

Temperature °C	Time at End of Second Order (min.)	Maximum Potential Yield (a)	"X" at End of Second Order	Percent of "a" During Second Order
47	60	0.1782	0.1221	69
57	60	0.1899	0.1473	80
67	60	0.1985	0.1663	84
77	60	0.2098	0.1863	89
87	60	0.2240	0.2077	94

The data after 60 minutes were found to be simple first order for the remainder of the extraction reaction. The first order equation to describe the portion of the reaction taking place after 60 minutes was:

$$\frac{dx}{dt} = k_1 (a-x) \qquad (3)$$

Integration and setting the limits as for equation (2)

$$\ln \frac{a}{a-x} = k_1 t \qquad (4)$$

The data for this portion of the reaction are plotted in Figure 12 to show the agreement of equation (4) to the data obtained.

Applying the absolute reaction rate theory to the second order and first order portions of the extraction process the rate constant, k' (or k_2 and k_1) would be of the form:

$$k' = \kappa \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} \qquad (5)$$

where κ = transmission coefficient (usually = 1.0)

k = Boltzman's constant

h = Planck's constant

T = absolute temperature (°K)

R = universal gas constant

$\Delta F^{\ddagger}$ = activation free energy (also can be expressed as = $\Delta H^{\ddagger} - T\Delta S^{\ddagger}$)

The rate constants were expressed by the expression

$$k' = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (6)$$

and plots of equation (6) are shown in Figure 13 and 14. Since $\ln \frac{k'}{T}$ is plotted against 1/T the slope is then $-\frac{\Delta H^{\ddagger}}{R}$ and the activation entropy $\Delta S^{\ddagger}$ can be obtained from the intercept. The values for the activation enthalpy and apparent activation entropy for the two portions of the reaction were:

	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
2nd order	8.7 kcal/mole	-44 e.u.
1st order	2.5 kcal/mole	-70 e.u.

With the values of the activation enthalpies obtained the extraction process appears to be under essentially physical control. Forces being affected if this is the case would include van der Waals or hydrogen bonding forces which are generally of the order of 1-10 kcal/mole. Freundlich and Gillings have demonstrated the breaking of the loose gel network of van der Waals bonds in gelatin-water[12] by ultrasonic waves. However, many other degradation and depolymerization reactions have also been effected by ultrasonic energy when the bonds involved were chemical bonds of 50-100 kcal/mole. Some polymers which have been depolymerized by ultrasonic waves are polystyrene[13], polyvinyl acetate, polyacrylates and nitrocellulose[14], and rubber[15].

An interesting and quite plausible explanation for the depolymerization of polystyrene solutions has been proposed by Crawford[16]. According to his calculations ultrasonic waves of 300 kc/s at 10 watts/cm^2 could easily furnish sufficient energy to break the C-C or C-O bonds. Forces from ultrasonic waves could be set up simply as friction between a polymer molecule and the surrounding liquid. In the case of polystyrene in toluene only 5 bonds in 1000 were broken at 70°C.

The structure of coal is, at best, very complex and the bonding forces are not well defined at present. There are, however, some general facts concerning the products of coal extraction, pyrolysis and hydrogenation which can be of great assistance in determining the types and magnitude of some of the important bonding forces in coal. Coal pyrolysis and coal

dissolution (solvent extraction) have been visualized by Wiser as similar processes, with similar reaction kinetics (second order) and activation enthalpies (35.6 kcal/mole and 28.8 kcal/mole respectively)[17]. The products resulting from coal pyrolysis and dissolution are high in aromatics, exhibiting even higher aromaticity than the original coal. From this and other work on the structure of coal the strongest bonds in the "coal macromolecule" appear to be aromatic carbon-carbon bonds. Aliphatic C-C bonds, C-O, C-H, and C-S bonding are also present and important in the coal structure[18]. Weaker forces such as van der Waals forces and hydrogen bonding would naturally be expected since coal can be considered as a polymer and other polymers containing C, H, S, N and O are at least partially held together by such bonding forces[19,20]. Pimental and McClellan[20] give values of hydrogen bond strengths of 3.0 to 7.7 kcal/mole.

The results of any kinetic study on a complex substance such as coal will indicate only average values of the activation enthalpies and entropies involved in the process being studied.

Since the value of "a", the maximum part of the coal extractable, varies systematically with temperature it appears that at any particular temperature the quantity (a-x) represents a potential in the form of a concentration. The rate at any particular time, t, depends only upon this concentration. As "x" approaches "a" the rate approaches zero. The value of "a" is much smaller when ultrasonic energy is not used in the extraction. From this study and others the effect of this energy appears to be the actual breaking of bonds in the coal structure which cannot be broken by the solvent. The breaking of these bonds then results in fragments from the coal which are soluble in the solvent liquid. Another possible effect of the ultrasonic energy is the transfer of kinetic energy

to the coal structure in such a way that would be the same as raising the "effective" temperature of the coal to some value much higher than the temperature measured by a thermometer or thermocouple in the solvent. According to Dognon and Simonot[21,22] the temperature of dispersed particles in an ultrasonic field is raised several degrees above the average temperature of the solution or suspension. The cavitation taking place in liquids subjected to ultrasonic waves (formation and violent collapse of small bubbles in the liquid due to pressure changes) has been credited with practically all observed chemical effects in liquid systems[9]. The violent collapse of cavitation bubbles may generate local pressures of thousands of atmospheres and/or local temperatures of hundreds of degrees above that of the environment[23]. The intensity of ultrasonic energy used in this study was several times that required to produce cavitation.

The results of this study may be interpreted in two different ways based on the above information:

(1) The extraction of coal with ultrasonic energy results in the dissolving of species present in the pores of the coal structure. Extraction also takes place by breaking van der Waals and hydrogen bonds in the coal structure. The extraction yield is higher with ultrasonic energy because these weak bonding forces are severed by the energy of the ultrasonic waves. The rate controlling step in the second order portion of the reaction is the reaction between the solvent molecules and the available van der Waals or hydrogen bonds in the coal. The activation enthalpy for this second order reaction is 8.7 kcal/mole. The second order dependence is most likely due to a rate controlling step involving both a solvent molecule and a van der Waals or hydrogen bond. When most of the extraction has taken place the slow step becomes solution diffusion

either of solvent molecules to the soluble species in the coal matrix or of dissolved extraction products from the coal into the bulk solution. This part of the reaction is first order and has an activation enthalpy of 2.5 kcal/mole.

(2) Assuming that the ultrasonic effect to the coal-tetralin system is to raise the "effective temperature" of the reacting species to some higher value leads to some very interesting conclusions. To obtain the "effective temperature" (T_e) corresponding to the measured temperatures of 47°, 57°, 67°, 77° and 87°C used in this study is not difficult if "a" values at these temperatures is used to obtain the temperature necessary for the same yield in a coal-tetralin system without ultrasonic energy. In previous work by Charlot[24] tetralin was used to extract Spring Canyon coal without ultrasonic energy. T_e values corresponding to 47, 57, 67, 77 and 87°C are found to be 258°, 261°, 263°, 267° and 269°C. Values of the activation enthalpies for the second order and first order portions of the reaction became 31.5 and 9.1 kcal/mole respectively. With these values the second order portion of the reaction would undoubtedly involve the same type of bond rupture that occurs with pyrolysis and dissolution as previously referred[17]. The first order portion of the reaction would then appear to be controlled by either the breaking of van der Waals and/or hydrogen bonds or possibly solution diffusion.

CONCLUSIONS

Kinetic data of solvent extraction with tetralin and ultrasonic energy over the temperature range 47-87°C have been obtained. The kinetic data indicate that the rate determining step for most of the process is a second order reaction probably involving tetralin molecules and van der Waals or hydrogen bonds in the coal. The activation enthalpy for this

second order reaction is 8.7 kcal/mole with an activation entropy of -44 e.u. The second order reaction is followed by a first order reaction with an activation enthalpy of 2.5 kcal/mole and entropy of -70 e.u. The rate controlling step for the first order portion of the reaction is probably solution diffusion. The high negative values for the activation entropies obtained are not surprising since similar results have been obtained by others working with complex reactants such as coal, coal tar, petroleum, and some pure aromatic compounds[25,26]. Such values are usually obtained when the number of reaction sites changes with the amount of reaction as would be the case for extraction[27].

No exact mechanism for the reactions taking place can be concluded. The interaction of the ultrasonic energy, tetralin, coal and environment cannot be completely understood until much more is known about such phenomena as the exact effects of ultrasonic waves upon organic solvents and suspended solids and extraction of coal; in particular how each type of bonding in coal is affected by the solvent molecules.

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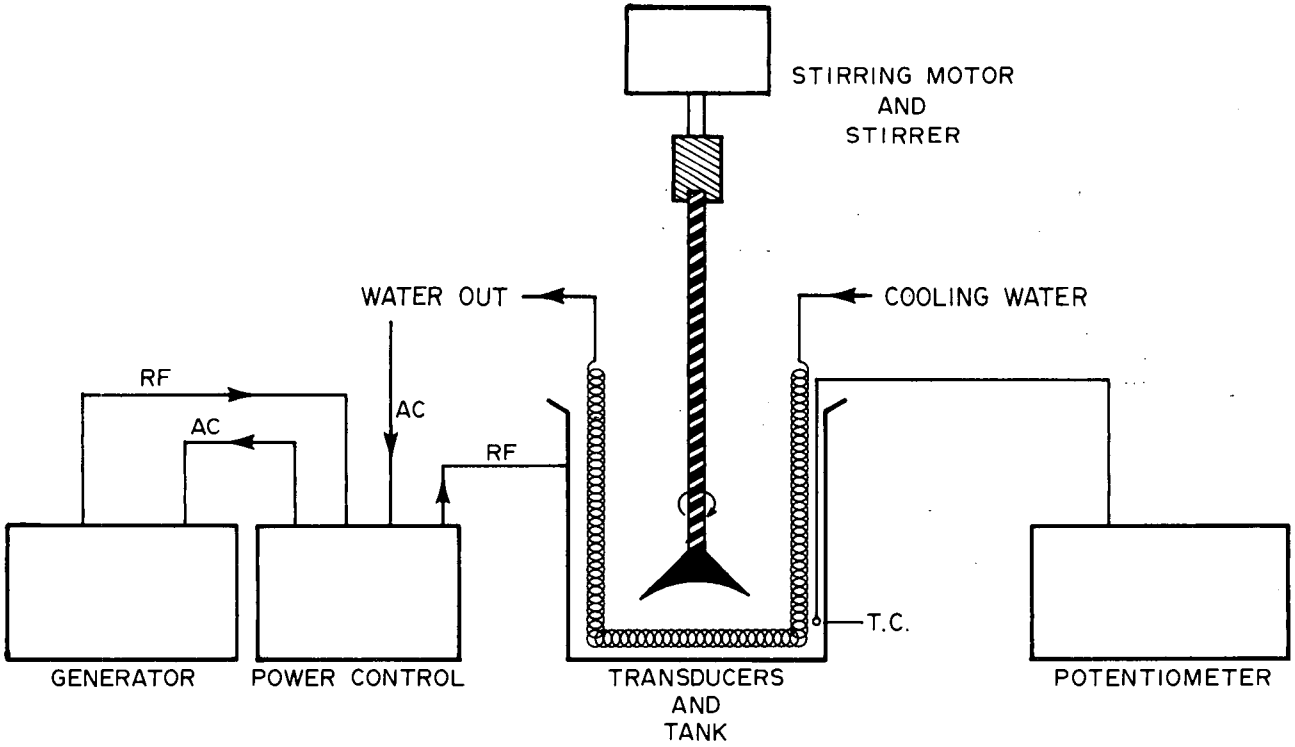

Figure 1. Schematic drawing of ultrasonic extraction apparatus.

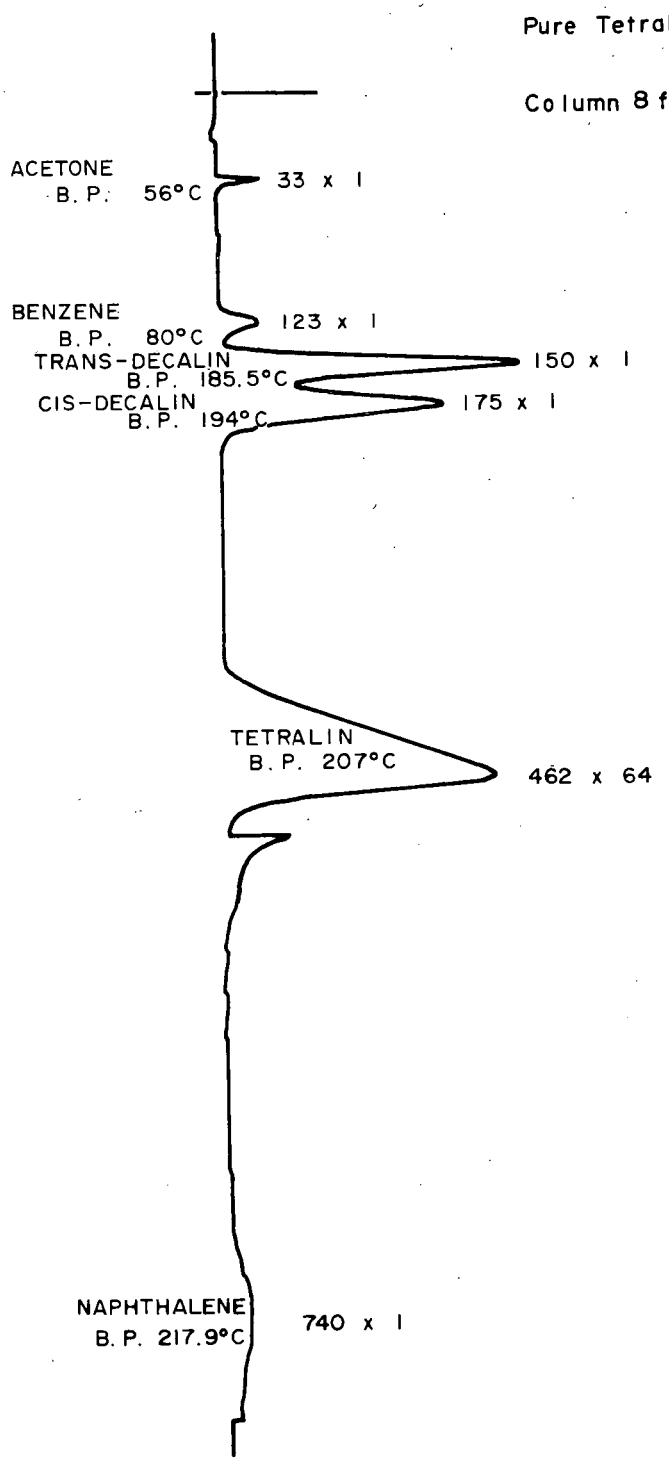

Figure 2. Chromatogram of Tetralin.

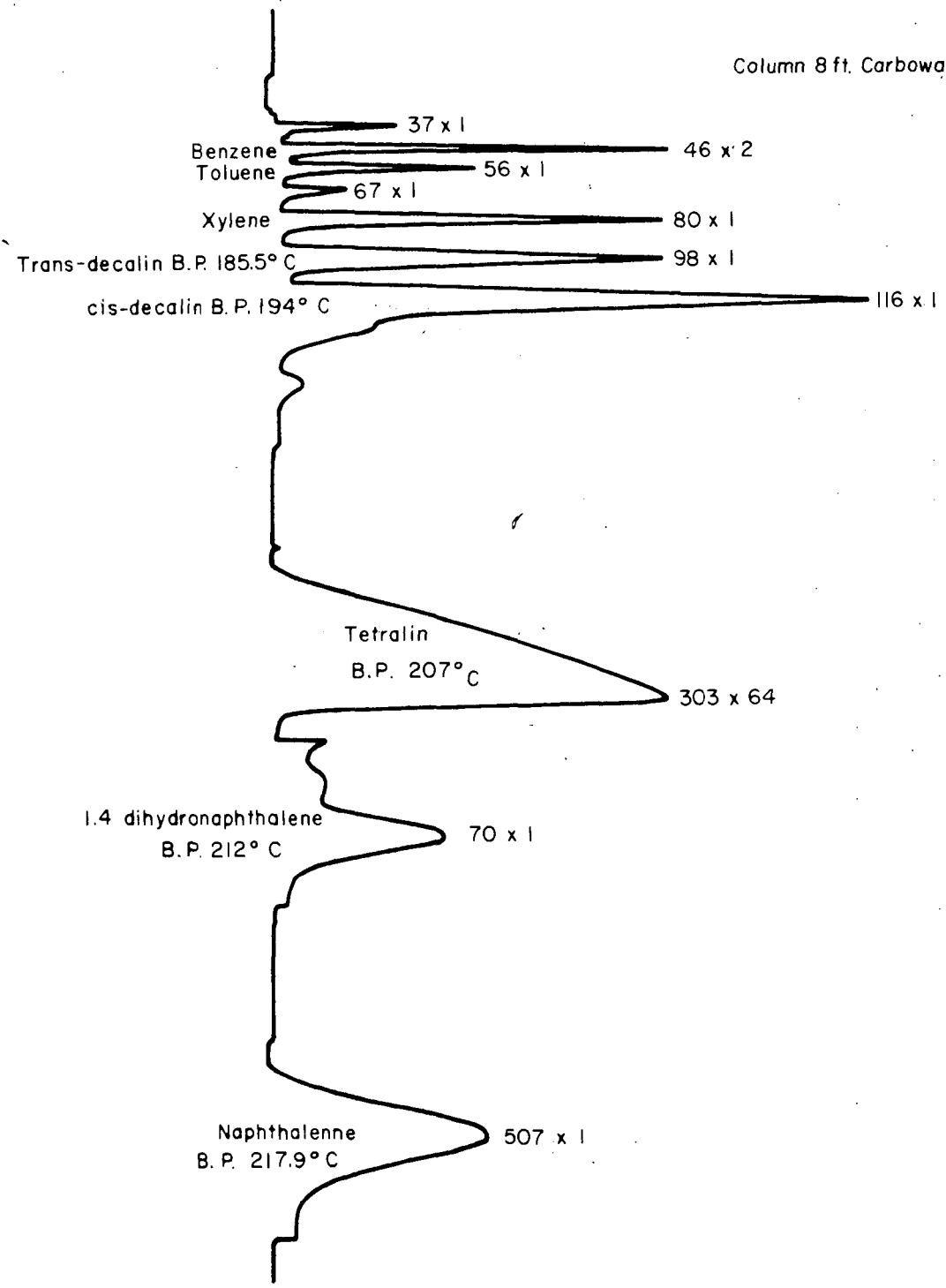

Fig. 3 Chromatogram of Tetralin Irradiated for 24 hours at 87°C at 3.75 watts/in^2.

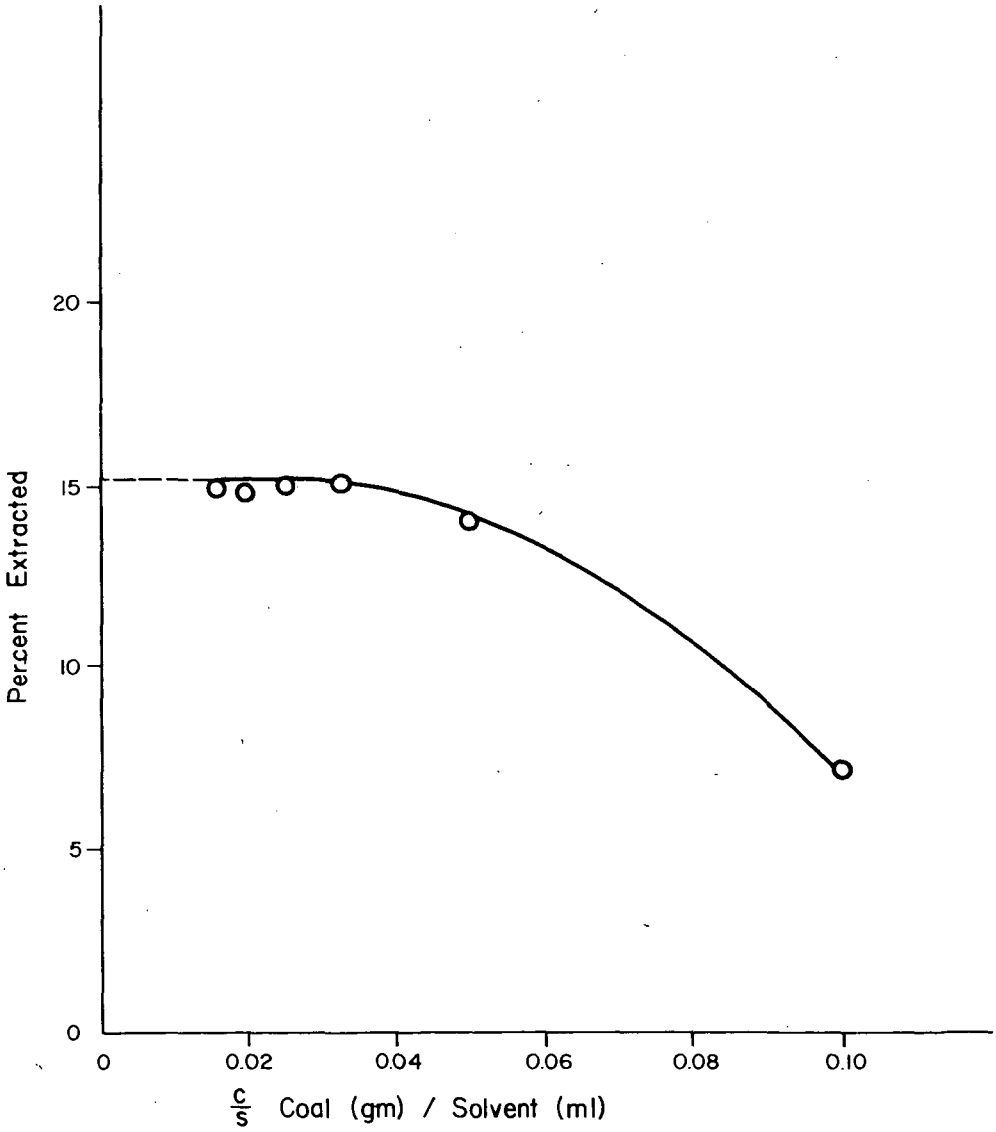

Fig. 4 Percent of extracted vs. $\frac{\text{coal}}{\text{solvent}}$ ratio
Temperature = 47°c; Time = 3 hours;
Coal size = −200 + 270 mesh
Solvent = tetralin

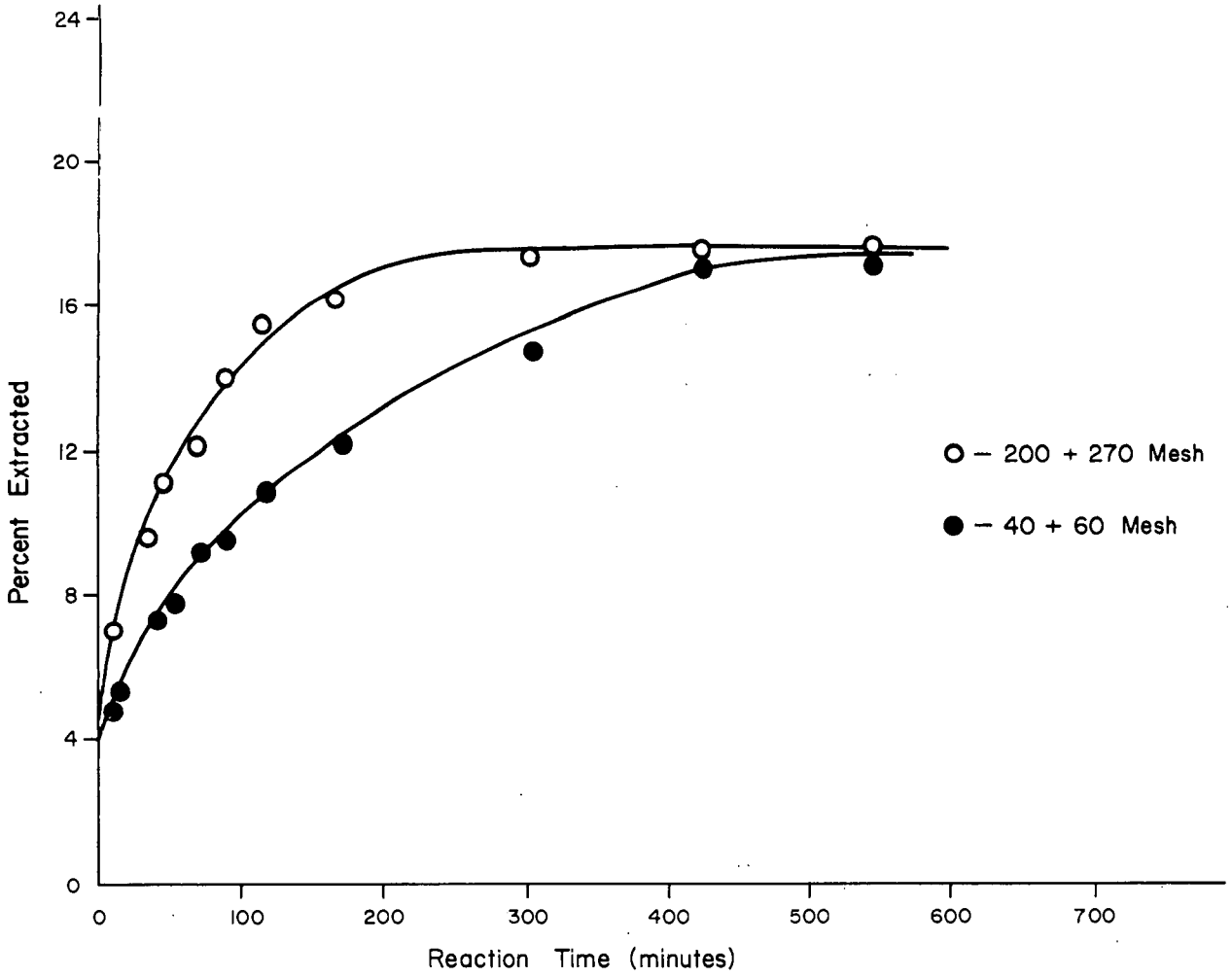

Fig. 5 −40 + 60 and −200 + 270 mesh coals. Effect of coal particle size on ultrasonic extraction with tetralin.

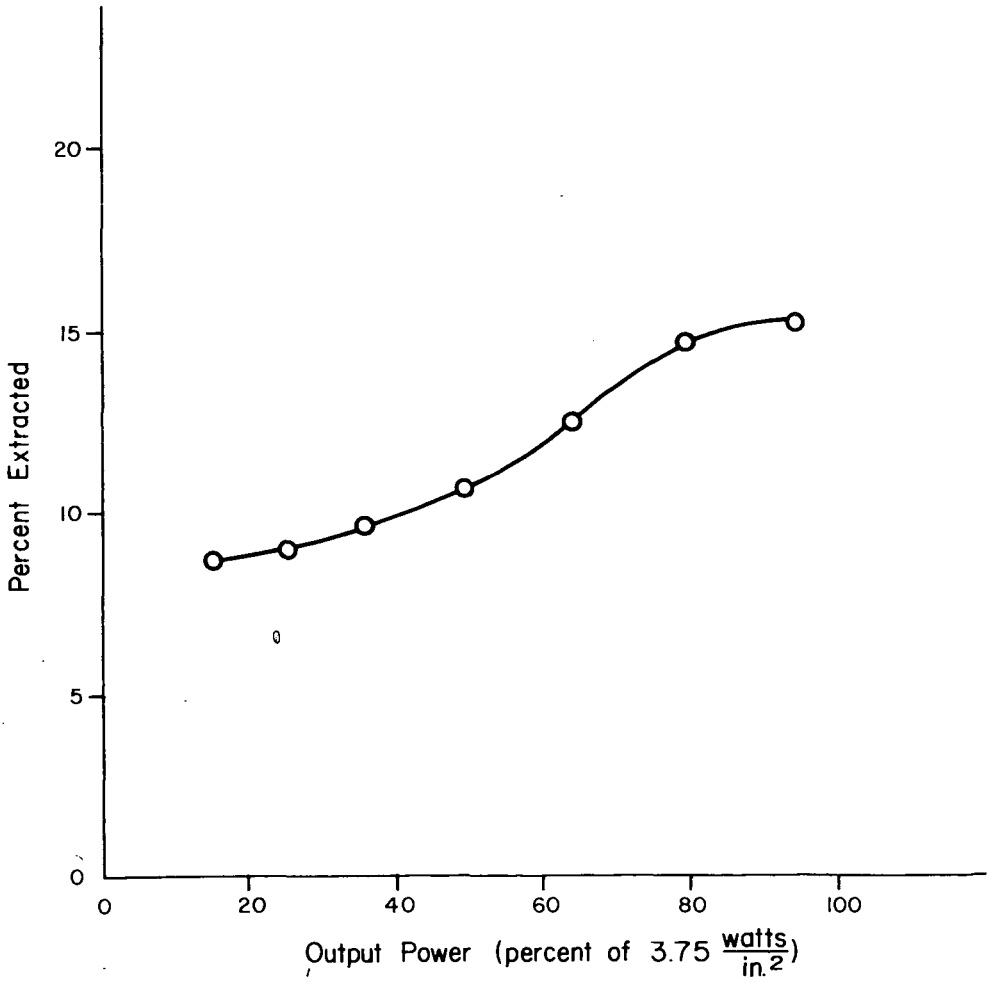

Fig. 6 Output vs. percent extracted at 47°c, and 3 hours reaction time in tetralin. Coal size = −200+270 mesh.

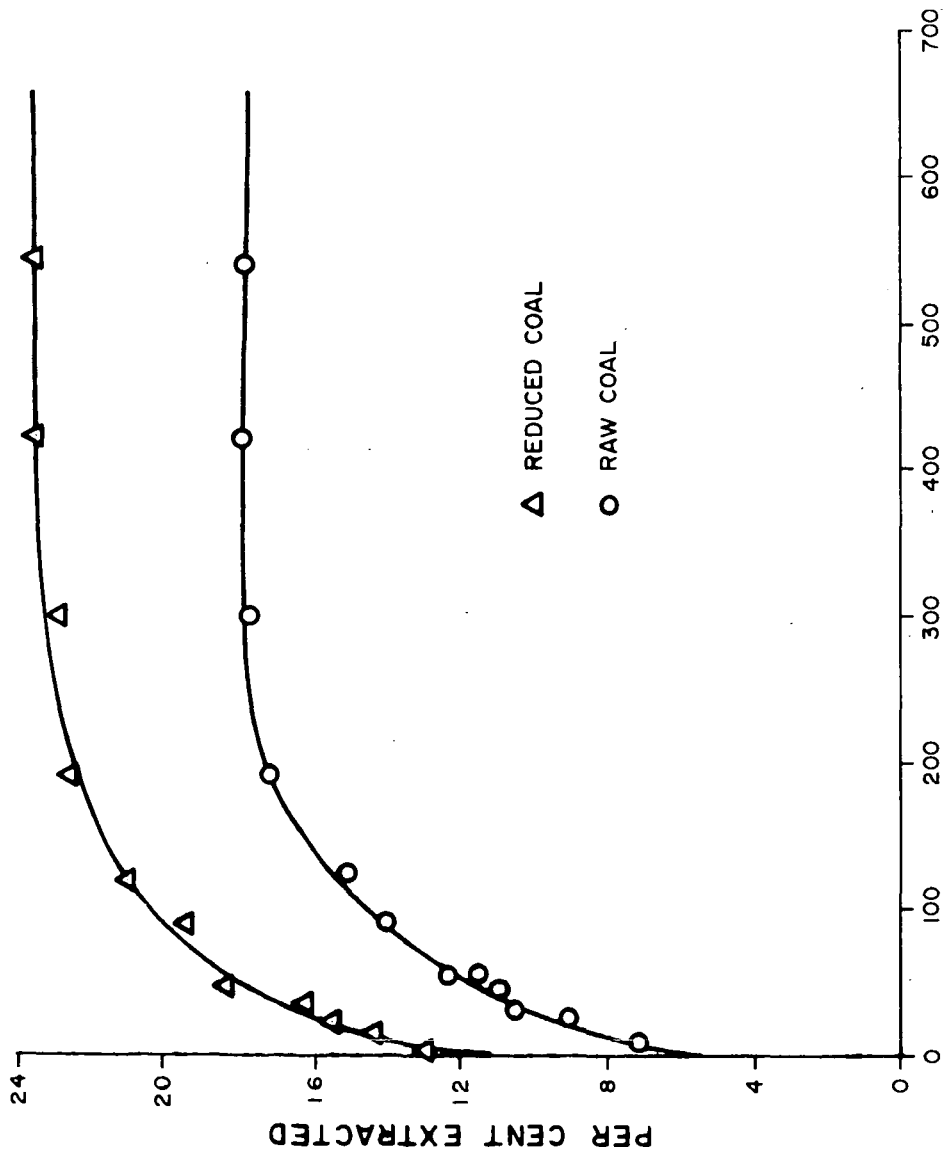

Fig. 7 Percent extracted versus time for raw and reduced coal.

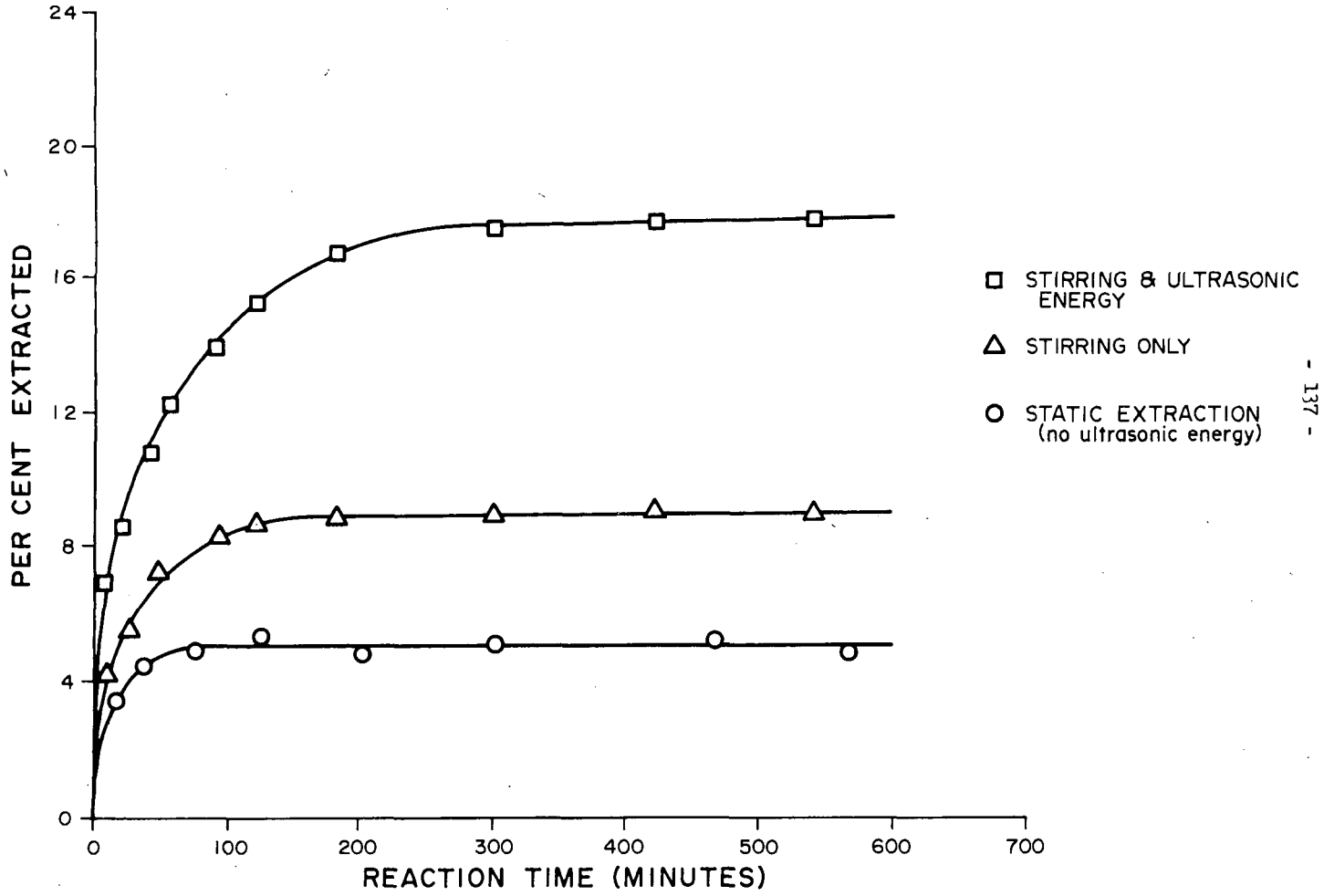

Figure 8. Percent extracted versus time at 47°C. Solvent = Tetralin, Power output = $\frac{3.75 \text{ watts}}{\text{in.}^2}$, Coal size = −200 + 270 mesh.

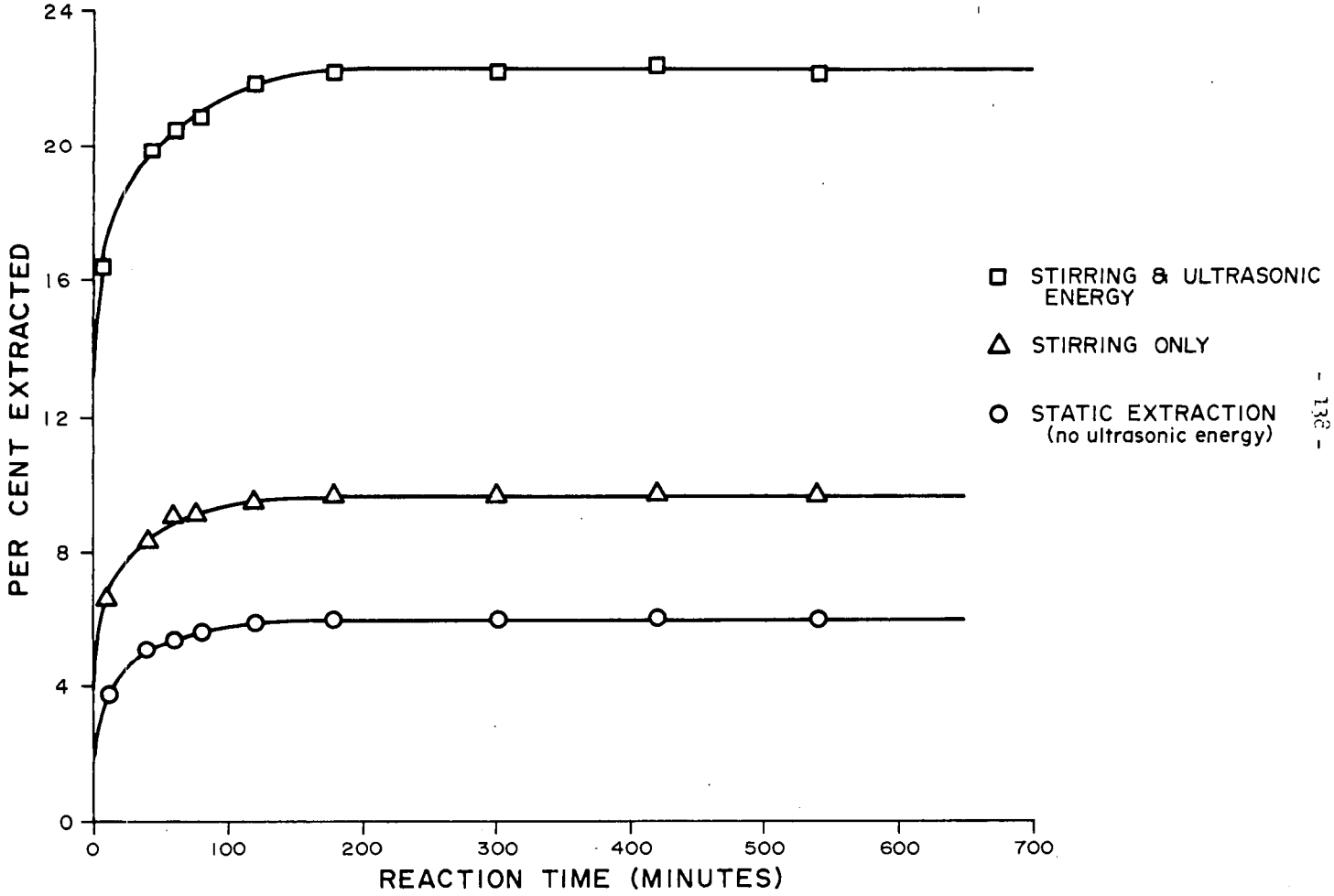

Figure 9. Percent extracted versus time at 87°C. Solvent = Tetralin, Power output = $\frac{3.75 \text{ watts}}{\text{inch}^2}$, Coal size = -200 + 270 mesh.

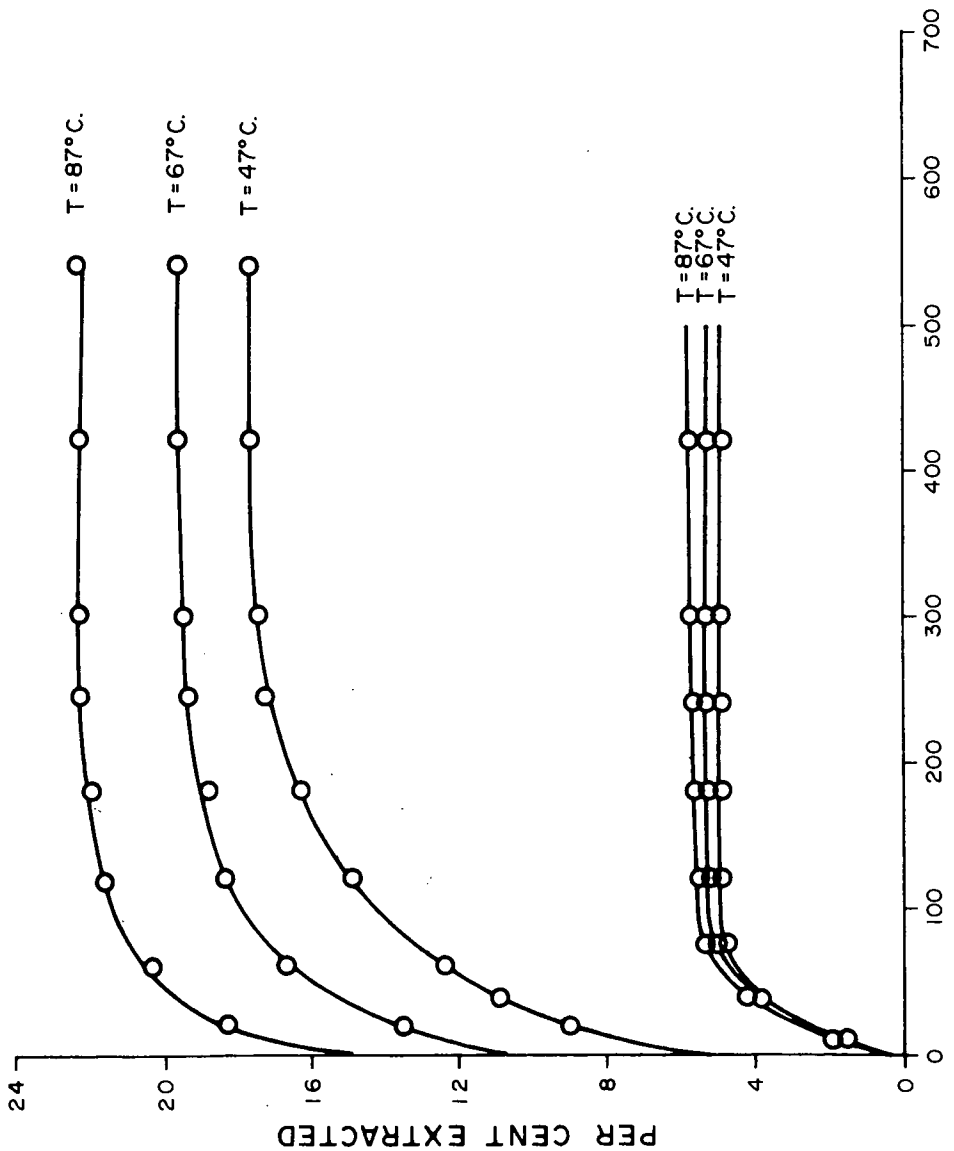

Figure 10. Kinetics of coal extraction with Tetralin.

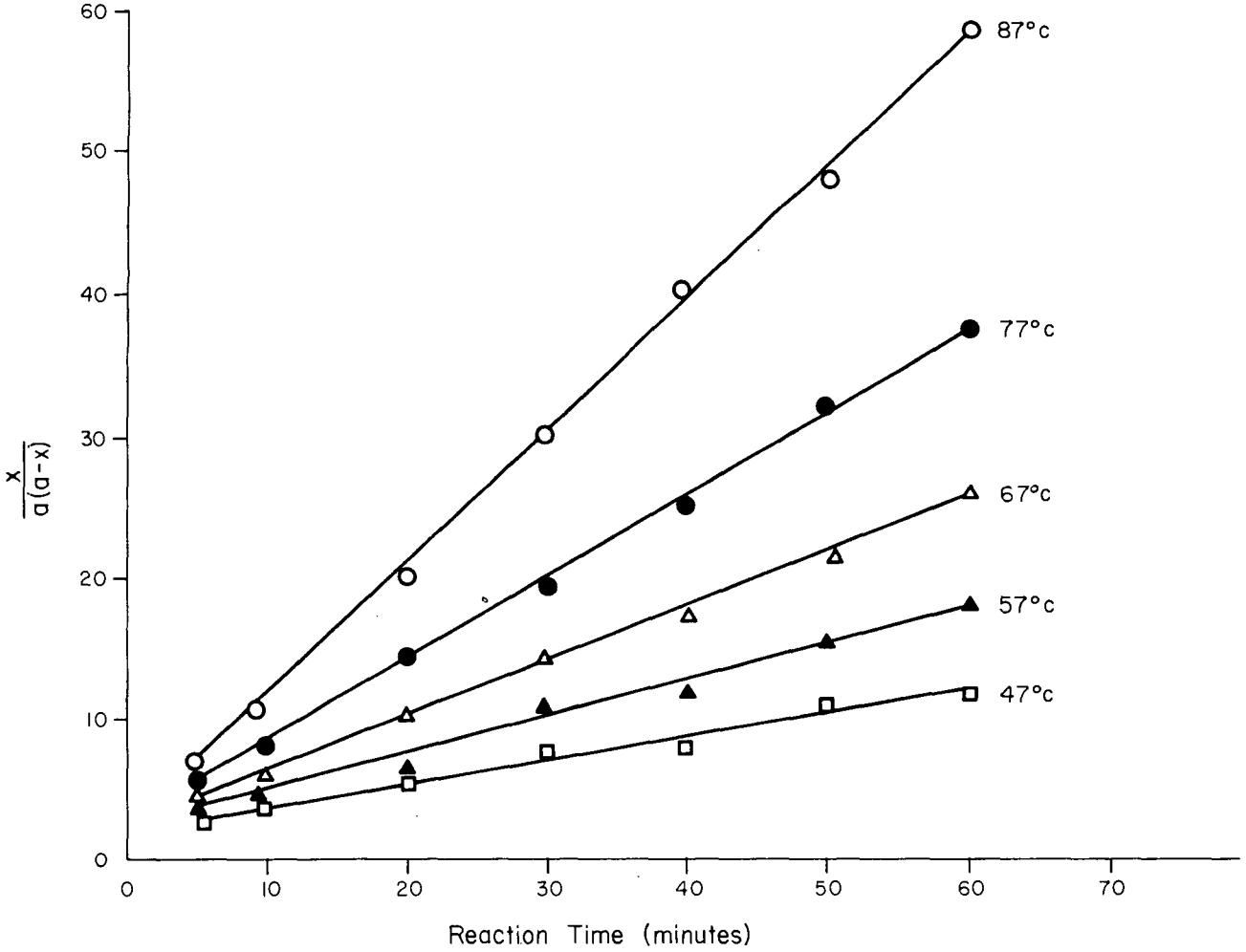

Fig. 11 Plot of $\frac{x}{a(a-x)}$ vs. time for second order reaction

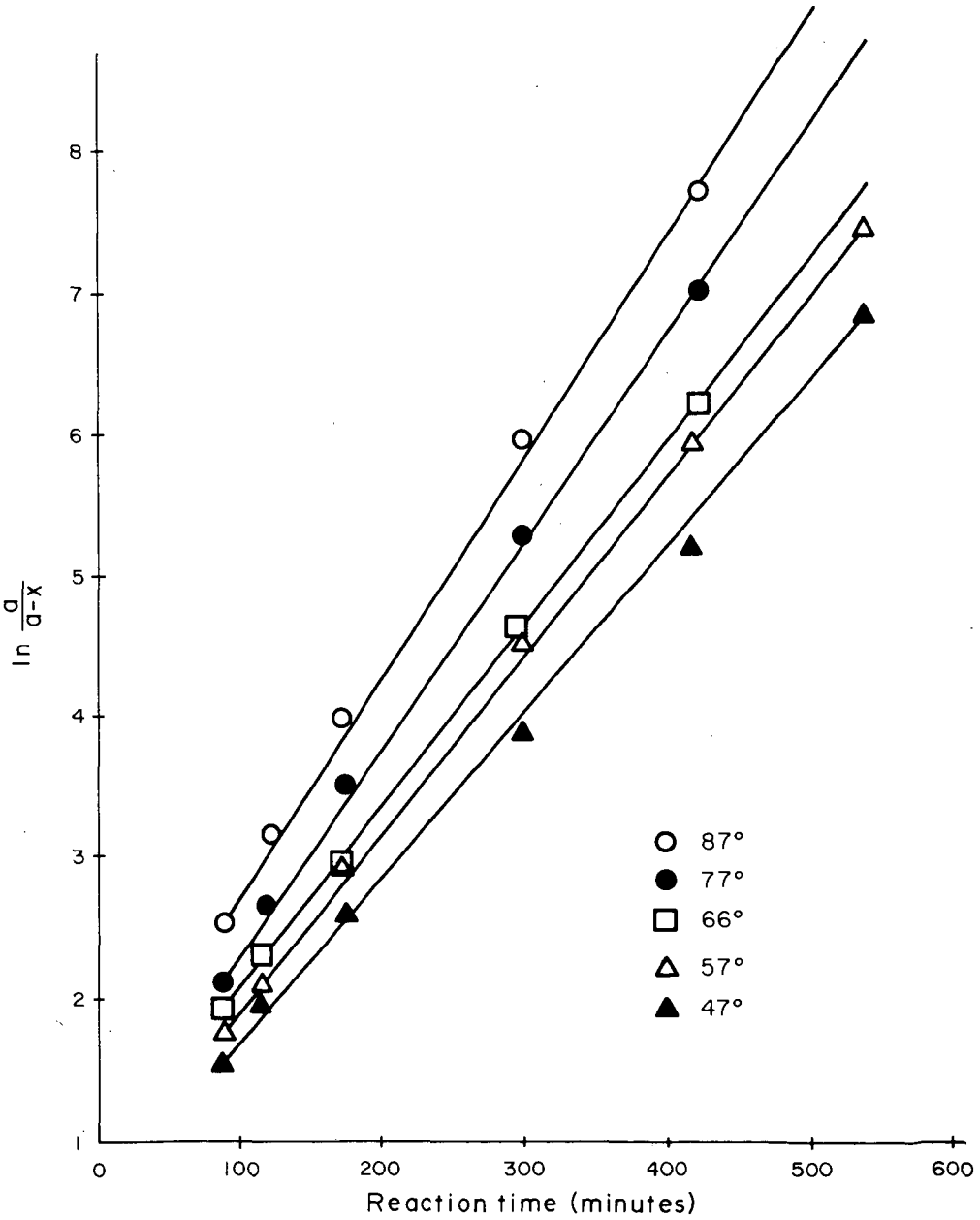

Fig. 12 Ln $\frac{a}{a-x}$ versus time for first order reaction.

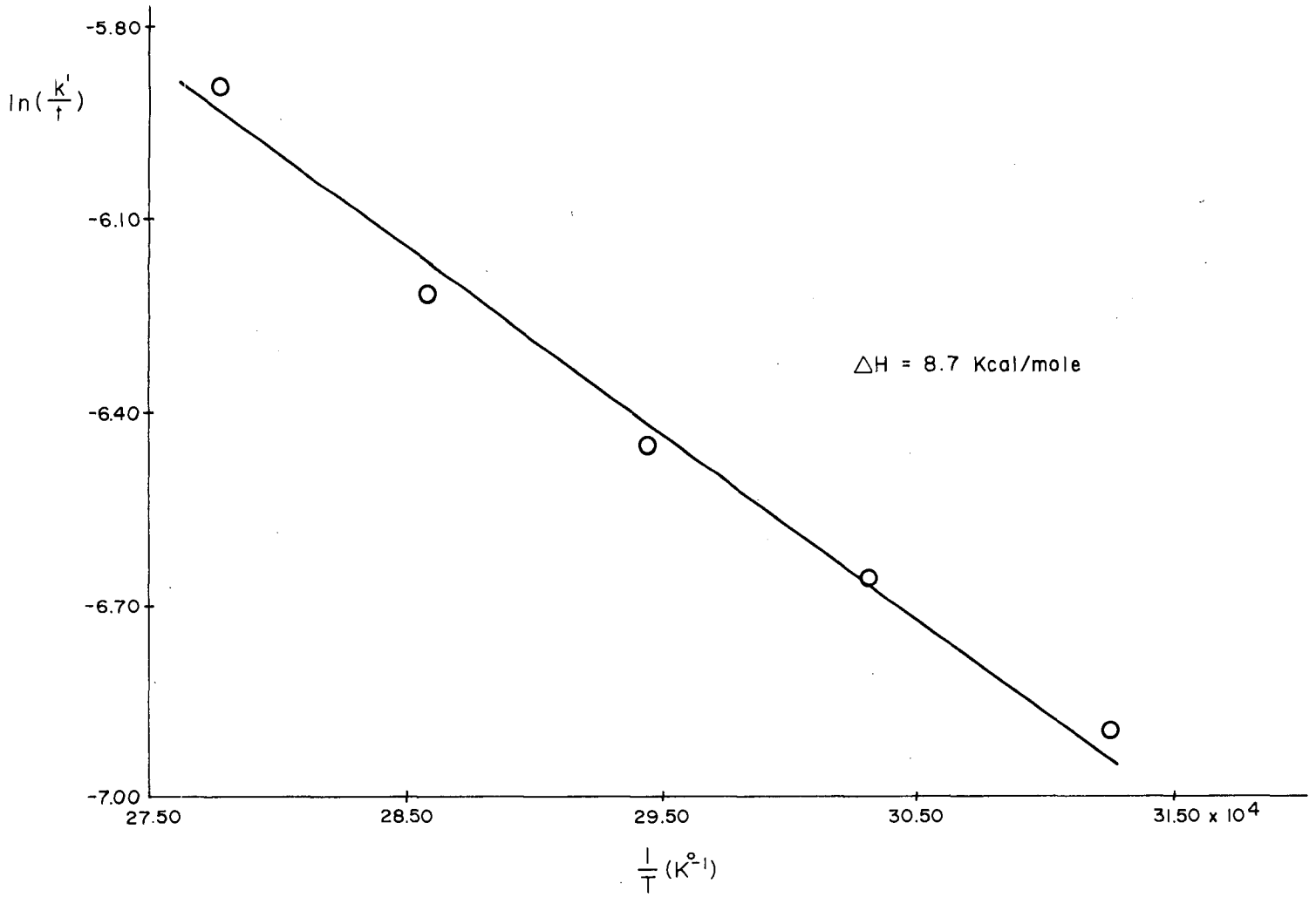

Fig. 13 Ln $\frac{k_2}{T}$ versus $\frac{1}{T}$ for evaluation of the activation enthalpy and entropy for second order portion of reaction.

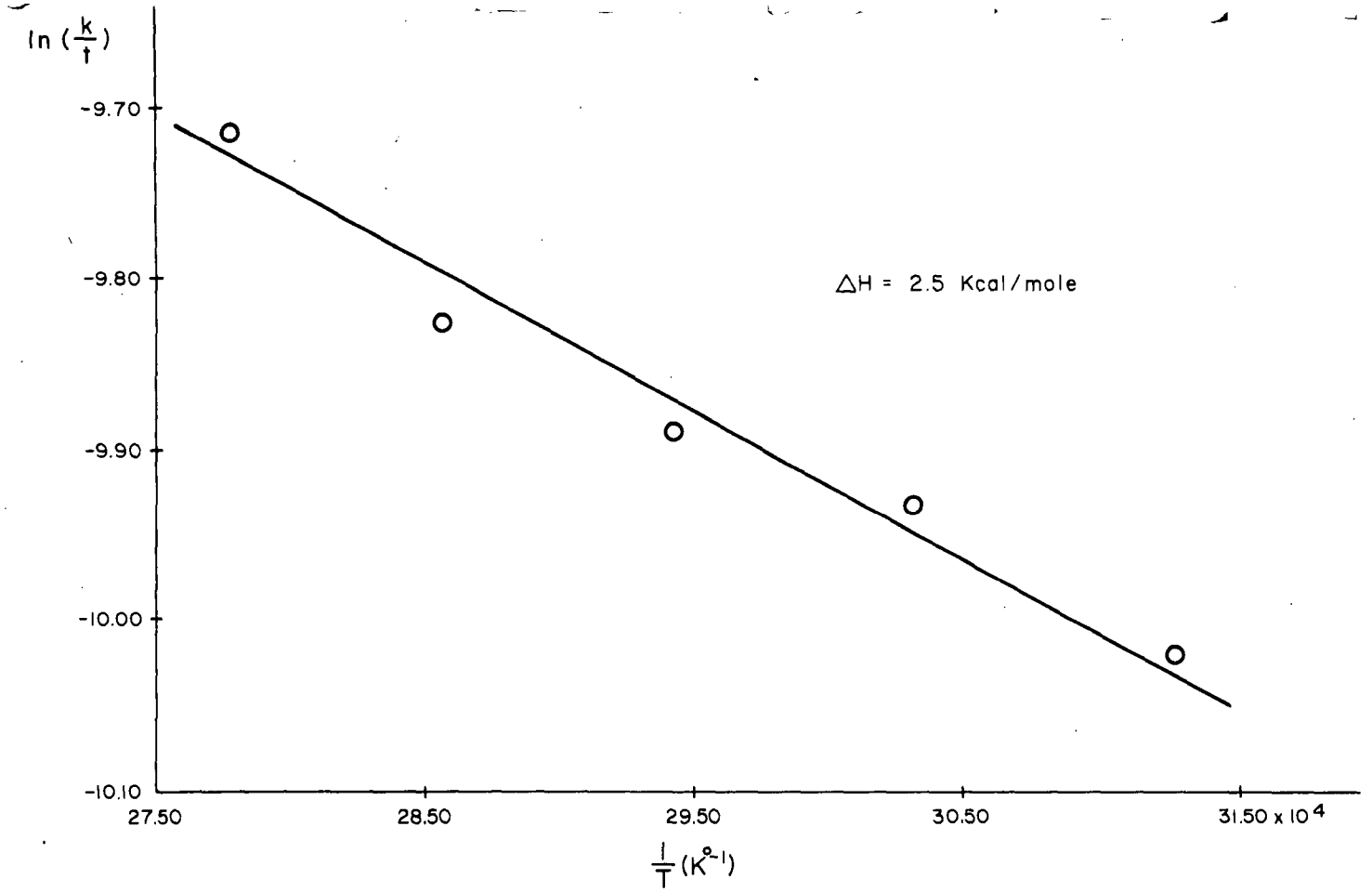

Fig. 14 Ln $\frac{k}{T}$ versus $\frac{1}{T}$ for evaluation of the activation enthalpy and entropy (first order reaction)